

Solicited Proposal for

Task 1.1

of

“Initial Data Analysis of CRPAQS Field Program Measurements”

California Regional PM₁₀/PM_{2.5} Air Quality Study

Submitted to:

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California Air Resources Board
Program Manager
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December 14, 2001

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Table of Contents

	<u>Page</u>
List of Figures	v
List of Tables	vi
1. Introduction.....	1-1
1.1 Objectives	1-1
1.2 Background	1-1
1.3 Evaluation Criteria.....	1-2
2. Scope of Work	2-1
2.1 Task 1.1.1 – Measurement Equivalence	2-1
2.2 Task 1.1.2 – Validity and Equivalence of Optical Measurements	2-2
2.3 Task 1.1.3 – Nitrate Loss during Sampling and Analysis	2-2
2.4 Task 1.1.4 – Effects of Gaseous Organic Adsorption/Desorption on Filter Organic Carbon Measurements	2-3
3. Technical Approach.....	3-1
3.1 Task 1.1.1 – Measurement Equivalence	3-9
3.2 Task 1.1.2 – Accuracy, Precision, and Validity of the Optical Measurements.....	3-18
3.2.1 Relationship between PM _{2.5} Mass and Light Scattering	3-18
3.2.2 Relationship between Continuous and Filter-Based Particle Light Absorption Measurements	3-19
3.3 Task 1.1.3 – Nitrate Loss during Sampling and Analysis	3-25
3.4 Task 1.1.4 – Adsorption of Gaseous Organic Carbon on Quartz-Fiber Filters.....	3-29
4. Management, Reporting, and Schedule	4-1
4.1 Project Management and Key Personnel	4-1
4.2 Reporting and Schedule	4-2
5. DRI Experience and Qualifications	5-1
5.1 Relevant Facilities and Expertise.....	5-1
5.1.1 Environmental Analysis Facility (EAF).....	5-1
5.1.2 Organic Analysis Laboratory (OAL)	5-1
5.2 Previous Projects	5-1
5.2.1 Central California PM ₁₀ /PM _{2.5} Air Quality Study (CRPAQS)	5-2
5.2.2 Fresno Supersite	5-2
5.2.3 Mexico City Particulate Study	5-3
5.2.4 Hong Kong Particulate Study.....	5-3

Table of Contents (continued)

	<u>Page</u>
6. Abbreviated Résumés – Key Personnel.....	6-1
6.1 Judith C. Chow	6-1
6.2 Steven D. Kohl.....	6-6
6.3 Matt P. Gonzi.....	6-8
6.4 Donald E. Lehrman.....	6-9
7. References.....	7-1
8. Cost Summary	8-1

List of Figures

	<u>Page</u>
Figure 1.1-1 Maps of monitoring sites in the CRPAQS network (the fall intensive study's 11 PM ₁₀ sites are not shown).	3-2
Figure 1.1-2 Diurnal variations of hourly black carbon concentrations from the single-wavelength (AETH1) and seven-color (AETH7) aethalometers for: a) average concentrations, and b) median concentrations, measured at 880 nm for every-sixth-day samples acquired at the Fresno Supersite during 2000.	3-17
Figure 1.1-3 Initial comparisons of particle scattering and PM _{2.5} concentrations at the Fresno First Street (FSF) urban and Helm (HELM) non-urban sites. Higher concentrations occurred during the winter and tend to deviate more from the linear regression relationship than those during other parts of the year. Nevertheless, there is a reasonably consistent relationship regardless of season.	3-24
Figure 1.1-4 Relationship between light transmission (b_{abs}) by densitometry from the Teflon-membrane filter and elemental carbon by Thermal/Optical Reflectance from the quartz-fiber filter for Federal Reference Method (FRM), Reference Ambient Air Sampler (RAAS), and Sequential Filter Sampler (SFS) samplers for samples acquired at the Fresno Supersite during 2000.	3-26
Figure 1.1-5 Monthly average non-volatilized and volatilized ammonium nitrate compared to PM _{2.5} mass concentrations from Andersen Reference Ambient Air Samplers (RAAS) and DRI Sequential Filter Samplers (SFS) at the Fresno Supersite during 2000.	3-28
Figure 1.1-6 RAAS sampling system configuration for method evaluation at the Fresno Supersite.	3-30
Figure 1.1-7 Temporal variations of RAAS speciation sampler quartz backup filter OC concentrations from: 1) non-denuded Teflon/quartz filter packs (TBK), 2) non-denuded quartz/quartz filter packs (QBK), and 3) denuded quartz/quartz filter packs, for samples acquired at the Fresno Supersite during 2000.	3-31

List of Tables

	<u>Page</u>
Table 1.1-1 Summary of CRPAQS anchor and satellite site aerosol measurements.	3-3
Table 1.1-2 Site Summary of CRPAQS sampling site locations, elevations, coordinates.	3-7
Table 1.1-3a Summary of collocated PM _{2.5} mass and chemical measurements at CRPAQS and compliance network sites.	3-10
Table 1.1-3b Summary of collocated PM ₁₀ mass measurements at CRPAQS and compliance network sites..	3-10
Table 1.1-4. Summary of in-situ continuous measurements acquired at CRPAQS anchor sites.	3-11
Table 1.1-5 Collocated comparison between filter-based and continuous PM _{2.5} measurements acquired between 01/01/00 and 12/26/00 at the Fresno Supersite.	3-13
Table 1.1-6 Summary of PM _{2.5} , PM ₁₀ , and nephelometer measurements in the CRPAQS anchor and satellite network.	3-20
Table 1.1-7 Cost summary for Task 1.1.	8-3
Table 1.1-8 Detailed cost distribution for Task 1.1.	8-4
Table 1.1-9 Summary of DRI's cost-sharing of non-labor-related expenses.	8-5

1. INTRODUCTION

1.1 Objectives

Task 1.1 intends to determine how measurements taken by different PM_{2.5} measurement methods and procedures can be used interchangeably for further data analysis. This is necessary because a variety of methods and procedures were applied during the field study, many of which represented emerging technologies. It is also necessary because no single particle measurement technology is perfect for all environmental conditions and aerosol compositions encountered during the study period. For example, PM_{2.5} mass was measured with single-channel Andersen Federal Reference Method (FRM) samplers, Andersen sequential FRM samplers, Andersen speciation samplers, Met One speciation samplers, DRI sequential filter samplers, Airmetrics Minivol samplers, continuous Met One beta attenuation samplers, and Tapered Element Oscillating Microbalance samplers. Nephelometer measurements of light scattering are intended to be used as a surrogate for PM_{2.5} when consistent and reliable relationships can be established. The nitrate, sulfate, elemental carbon, and total carbon components of PM_{2.5} were also quantified by several different methods. These analyses are a pre-requisite for all of the other data analysis tasks involving PM measurements as other data analysts will need this information to explain or qualify many of their observations that integrate the measurements acquired from different measurements. Initial emphasis will be given to the winter 2000/2001 period for which the largest number of instruments was deployed and which will be the most intensely studied period. Evaluation of PM₁₀ derived from nephelometer particle light scattering will be emphasized for the fall study period around Corcoran. For the summer, PM_{2.5} relationships to light scattering will be studied at the Edwards AFB anchor site.

The objectives of Task 1.1 are:

- Establish relationships between PM_{2.5} mass and light scattering measurements as well as between PM_{2.5} elemental carbon and light absorption measurements.
- Estimate the extent of nitrate volatilization and organic artifacts.
- Determine the causes of differences in collocated measurements.
- Determine the equivalence, comparability, predictability, and bias of collocated measurements and compare research monitoring systems with Federal Reference Method (FRM) samplers.

1.2 Background

The California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS) is a multiyear effort to understand the causes of elevated suspended particulate concentrations and to evaluate ways to reduce them in central California (Watson et al., 1998b). The San Joaquin

Valley (SJV) in central California frequently experiences elevated PM₁₀ concentrations during the fall and winter months. Past studies (Chow et al., 1992b, 1993a, 1996, 1998) have shown that wintertime PM concentrations were primarily in the PM_{2.5} size fraction, while during the remainder of the year PM₁₀ consisted of nearly equal parts of PM_{2.5} and coarse particles (PM₁₀ minus PM_{2.5}).

Higher annual-average PM_{2.5} and PM₁₀ concentrations were found in urban areas than in non-urban areas (Chow et al., 1992b). While primary (emitted directly) chemical constituents such as elemental carbon (EC) and crustal components (e.g., silicon, iron) displayed spatial variations, the concentrations of inorganic secondary aerosols such as NH₄NO₃ and (NH₄)₂SO₄ were much more uniform throughout the valley.

Surface wind speeds during winter in the SJV are very low, often <1 m/sec, and surface wind directions are variable. Surface transport distances estimated from these wind speeds are insufficient to account for the mixing of non-urban NH₃ emissions with urban NO_x emissions for the formation of secondary NH₄NO₃ (Smith and Lehrman, 1994). EC concentrations in the cities are more than three times the non-urban concentrations on the same day (Chow et al., 1993a). These observations suggest that particle concentrations in the SJV are determined by regional-scale interaction of source emissions, chemical transformation, vertical mixing, horizontal transport, and deposition.

A conceptual model is needed to describe how primary particle emissions and gaseous precursors from urban and non-urban areas interact with each other under the stagnant, moist, and foggy conditions often present in the SJV during winter. CRPAQS provided the time-resolved aerosol measurements at urban and non-urban sites, coupled with surface and upper-air meteorological measurements, to formulate this conceptual model and to evaluate what area and temporal periods this network represents.

1.3 Evaluation Criteria

The combination of staff, current research projects, facilities, and cost structures of DRI will make this proposal especially attractive to the Technical Committee. The evaluation criteria include: 1) technical approach, 2) expertise of the proposed staff, 3) related previous experience, and 4) cost-effectiveness.

The technical approach is presented in Section 3 of this proposal. This approach provides an overview of PM and precursor gas measurements, sampling locations and durations for the annual program as well as fall and winter intensive studies, and approaches to evaluating the equivalence, comparability, and predictability of different measurement methods.

The principals proposed for DRI are unsurpassed in terms of their demonstrated expertise in this type of study. Dr. Judith Chow at DRI has been a major participant in many California air quality studies including:

- *In California's central valley:* the 1988-89 Valley Air Quality Study (VAQS; Chow et al., 1992b, 1993a), 1990 San Joaquin Valley Air Quality

Study/Atmospheric Utility Signatures, Predictions, and Experiments (SJVAQS/AUSPEX; Fujita et al., 1995; Chow et al., 1996), 1995 San Joaquin Valley Integrated Monitoring Study (IMS95; Chow et al., 1998), 1999-2001 CRPAQS aerosol measurements, and 1999-2003 Fresno Supersite Study (Watson et al., 2000; Watson and Chow, 2001a, 2001a);

- *Along the Pacific coast of California:* the 1989 Santa Barbara PM₁₀ Study (Chow et al., 1996) and 1991-92 Bay Area PM₁₀ Study (Chow et al., 1995); and
- *In southern and southeastern California:* the 1987 Southern California Air Quality Study (Chow et al., 1994a, 1994b; Fujita et al., 1994; Watson et al., 1994a), 1988 Rubidoux/Riverside Neighborhood-Scale Study (Chow et al., 1992a), and 1992-93 Imperial Valley/Mexicali PM₁₀ Study (Chow et al., 2000; Chow and Watson, 2001; Watson and Chow, 2001b).

The selected peer-reviewed references attest to her past experience and qualifications.

Mr. Steven Kohl has over five years of experience working in and managing DRI's Environmental Analysis Facility. He supervised EAF's staff during the CRPAQS field studies; coordinated field/laboratory logistics during the 14 months of CRPAQS field operations; and has been responsible for assembling, processing, validating, and reporting the Level I aerosol database for CRPAQS and other air quality studies such as the Texas PM_{2.5} Characterization Study, Upper Ohio River Valley Study, Fresno and St. Louis supersite studies, Mid-Atlantic Air Quality Study, and Las Vegas Air Quality Study. The EAF staff worked around the clock during the 2000-01 Christmas/New Year holiday season to ensure that adequate supplies of sampling media and sampling equipment components were available at each of the 53 sampling locations during the 2000-01 CRPAQS winter intensive study period.

Mr. Don Lehrman, senior scientist and principal of T&B Systems, Santa Rosa, CA, has extensive knowledge of the satellite network and meteorological characteristics in the central valley. He has been the principal investigator or a major participant in numerous field measurement and analysis programs over the past 25 years. Mr. Lehrman will serve as an independent reviewer and provide input on siting characteristics and the representation of the site.

DRI's staff have extensive experience in performing spatial and temporal analysis and modeling of concurrent measurements from 20 to 30 sampling locations. The principal investigators and the supporting staff are well acquainted with the sampling, analysis, and modeling aspects of the proposed study.

DRI has conducted or participated in a number of methods comparison and evaluation studies (e.g., Mathai et al., 1990; Chow et al., 2001a; Watson and Chow, 2002) that are similar to the one proposed here. The proposed team demonstrates experience and participation in nearly every one of the major air quality studies conducted over the past two decades. The principal investigator's experience includes major roles in over a dozen major

aerosol and visibility monitoring studies that have included similar comparisons. Data analysis methods are specified in the technical approach in Section 3.

The proponent's ability to carry out the proposed work within the time and budget constraints is outlined in Section 5. A key to maintaining the schedule is that DRI staff are well acquainted with the aerosol measurements taken in the San Joaquin Valley as well as the sampling site locations and surrounding environs. DRI scientists (Dr. Judith Chow, Dr. John Watson, Dr. Douglas Lowenthal, Dr. John Bowen, Mr. Steven Kohl, Mr. Matt Gonzi, Mr. Dale Crow) have been actively working on field operations, data analysis, and air quality modeling for the Fresno Supersite since May 1999. The objectives of the Fresno Supersite project are to: 1) test, evaluate, and compare non-routine and existing monitoring methods; 2) acquire data bases to evaluate relationships between aerosol properties, co-factors, and observed health endpoints; and 3) support regulatory agencies in the development of cost-effective emissions reduction implementation plans. The Fresno Supersite research, which is sponsored through a cooperative agreement with the U.S. Environmental Protection Agency (U.S. EPA) and the National Oceanic and Atmospheric Administration (NOAA), is directly related to the data analysis to be performed for CRPAQS; as such, substantial cost benefits can be achieved.

This project can and will be given priority. The key personnel are fully dedicated to this project. They have been involved in air quality measurements in the San Joaquin Valley for more than a decade, and they have always placed this local interest above other more remote opportunities that have presented themselves. DRI is a state agency and is backed by the University and Community College System of Nevada and the State of Nevada. DRI's financial stability as a unit of the University of Nevada System is healthy, long-term, and growing.

With respect to compensation for contracted services, DRI is a non-profit entity and records no financial gain from revenues collected from this or any other project. DRI's interest in this project derives from the unique opportunities it offers to advance our fundamental knowledge about the spatial scales represented by particle samplers. The project has been budgeted to take advantage of different cost structures of the project team. Though DRI must adhere to certain rules established by the Federal Government for cost recovery, it is amenable to alternative arrangements that reduce costs to the sponsors.

Finally, DRI, as part of the State University System, maintains a policy of non-advocacy. DRI participates only in the research aspects of air pollution studies. Results from these studies are presented objectively to decision makers without regard to the sensitivities of special interests or political pressures. DRI enjoys the reputation of working equally well with the U.S. EPA, various state and local agencies, and with commercial interests in the development of technical guidance and databases for regulatory analysis. Wherever possible, DRI collaborates with, rather than competes with, the private-sector environmental consulting industry to obtain the best combination of skills, lowest costs, and greatest benefit to the project sponsor and to DRI's goal of technology transfer between university research and environmental assessment.

2. SCOPE OF WORK

Task 1.1 of the Request for Proposal includes six sub-questions:

- QUESTION 1.1-1 What is the comparability and equivalence among collocated sampling methods, what are the biases of one instrument with respect to others, and how can these biases be minimized?
- QUESTION 1.1-2 What are the accuracy, precision, validity, and equivalence of light extinction, scattering, and absorption measurements?
- QUESTION 1.1-3 How much ammonium nitrate is lost in the sampling and analysis process?
- QUESTION 1.1-4 How much organic carbon is lost from samples due to volatilization and how much organic carbon is really due to adsorption of vapors on filters?
- QUESTION 1.1-5 How well do research monitoring systems compare to compliance monitoring reference methods?
- QUESTION 1.1-6 To what extent do instrumental differences impede the detection of actual differences between measurements at different times and locations?

The following scope of work is structured to answer each of the questions as noted. Each of these subtasks supplies information to address primary **QUESTION 1: HOW WELL DO PM AND METEOROLOGICAL MEASUREMENT SYSTEMS QUANTIFY MASS CONCENTRATIONS, PARTICLE SIZES, CHEMICAL COMPONENTS, AND METEOROLOGICAL FEATURES?**

2.1 Task 1.1.1 – Measurement Equivalence

addresses: QUESTION 1.1-1. Comparability and equivalence among collocated measurements?
QUESTION 1.1-2. Accuracy, precision, validity, and equivalence of optical measurements?
QUESTION 1.1-5. Comparability between research and compliance monitoring methods?
QUESTION 1.1-6. Instrumental differences vs. actual differences between measurements?

From written measurement reports and interviews with site operators, summarize in a table the PM_{2.5} measurement configuration at each site. Include information about sampling inlets, filter media, location of instrument (e.g., rooftop, inside heated or unheated shelter), filter handling/shipping, and sample processing location. Briefly summarize published information on inlet cut-points and flow rates, effects of differences in operational procedures, and other comparisons. Form hypotheses about the conditions under which comparability is expected and unexpected. Assemble the continuous hourly data for PM mass, ions, and carbon. Assemble the 5 times/day and once/day filter pack data for ammonia and PM mass, b_{abs}, elements, ions, and carbon. Examine pairwise comparisons, frequency

distributions, correlations, scatter plots, and regression coefficients among collocated continuous, collocated filter-based, and collocated continuous vs. filter-based measurements and identify outliers for investigation. Calculate collocated precision and root mean squared precision. Calculate student t-statistics to determine the degree of equivalence among different measurements. Examine the largest deviations between different methods and explain them in terms of the aerosol composition, environmental factors such as temperature and humidity during sampling, and the sampling method. For each sampler comparison pair, tabulate consistent biases that should be considered when comparing $PM_{2.5}$ measurements from different locations using different measurement methods.

2.2 Task 1.1.2 – Validity and Equivalence of Optical Measurements

Summarize by site the precisions estimated from zero and span tests for Radiance nephelometers. Calculate linear regression relationships between 24-hour average nephelometer readings and $PM_{2.5}$ where the instruments are collocated. Examine outliers with respect to nephelometer and ambient temperature and humidity levels. Create a table of “predictability” functions that can be used to estimate $PM_{2.5}$ mass from particle scattering measurements. For nephelometers not collocated with $PM_{2.5}$, assign and justify a regression relationship from other sites with collocated measurements. Create a data base of “equivalent” $PM_{2.5}$ concentrations for the entire nephelometer data base, including periods between the sixth-day collocated sampling. Describe how this inferred $PM_{2.5}$ data base can be used for other analyses and submit it to the CRPAQS data management system. Repeat these equivalence tests for the PM_{10} vs. particle light scattering measurements for the fall Corcoran study period. Where different nephelometers are collocated, compare their particle scattering measurements and attribute differences to instrument geometry, aerosol particle size variations, and humidity differences. Tabulate comparison statistics for the 880 nm measurements of particle light absorption with measurements from the single- and seven-color aethalometers where they are collocated. Compare the aethalometer measurements with continuous thermal evolution carbon measurements and filter transmission (b_{abs}) measurements on Teflon-membrane filters and filter elemental carbon measurements on quartz-fiber filters by thermal/optical reflectance. Explain differences and systematic biases in terms of differences in meteorology, particle composition, and operating methods.

2.3 Task 1.1.3 – Nitrate Loss during Sampling and Analysis

Using samples with denuders and backup filters, quantify the amount of nitrate volatilization during sampling for different seasons and in different environments. Examine temporal and spatial variations of nitrate volatilization and estimate the extent to which $PM_{2.5}$ mass is not measured gravimetrically. Calculate comparison statistics for particle nitrate measured by FRM, speciation, SFS, denuder difference (for 15 episode days only), Minivol and flash volatilization nitrate measurements. Determine the extent to which differences in volatilized nitrate measurements are attributable to differences in sample changing schedules. In particular, estimate the extent to which Minivol nitrate at satellite sites, which had no denuder, is overestimated when the backup filter nitrate is added. Calculate comparison statistics for nitric acid determined by denuder difference and continuous measurement methods. Determine the extent to which the continuous measurements can be considered

valid to determine diurnal variation for the 15 episode days and for the intervening days during the winter sampling period.

2.4 Task 1.1.4 – Effects of Gaseous Organic Adsorption/Desorption on Filter Organic Carbon Measurements

Summarize results from previous studies of positive and negative organic carbon artifacts determined in central California and elsewhere. For measurements at the Fresno supersite, compare front- and backup-filter organic carbon (OC) for denuded and non-denuded sample streams. Estimate what this bias is and determine how it affects OC measurements for diurnal samples of shorter duration (as low as 3 hours) taken during the 15 intensive sampling days. Calculate comparison statistics for filter and continuous thermal evolution carbon measurements.

3. TECHNICAL APPROACH

A comprehensive aerosol monitoring network (shown in Figure 1.1-1) has been established as part of CRPAQS to improve understanding of emissions and atmospheric processes that influence particle formation and distribution in the SJV and to develop and demonstrate methods useful to decision makers in formulating control strategies for attaining the Federal and state PM_{2.5} and PM₁₀ standards in central California.

Measurements of precursor gases and PM taken during CRPAQS included: 1) gaseous NH₃ and HNO₃ by the denuder difference method with DRI medium-volume sequential gas samplers (SGS) at the anchor sites; 2) PM_{2.5} and NH₃ by DRI sequential filter samplers (SFS) equipped with Bendix 240 cyclone inlets and preceding nitric acid denuders at the anchor sites; and 3) PM_{2.5}, PM₁₀, and NH₃ by battery-powered Airmetrics Minivol samplers at the satellite sites. PM_{2.5} and PM₁₀ mass, filter transmission (b_{abs}), 40 elements (Na to U; Watson et al., 1999), ions (Cl⁻, NO₃⁻, SO₄⁻, Na⁺, K⁺, NH₄⁺; Chow and Watson, 1999), volatilized NO₃⁻, and seven-fraction organic and elemental carbon were acquired. Table 1.1-1 summarizes the measurements acquired during CRPAQS.

The annual anchor network includes 14 months of daily PM_{2.5} sampling between 12/03/99 and 02/03/01 at two major urban centers (Fresno [FSF] and Bakersfield [BAC]) to represent community human exposure, and at one intrabasin gradient and vertical gradient site (Angiola [ANGI]) located in a flat field ~85 km south/southeast of Fresno to represent environments with minimal influences from urban or non-urban sources. Additional anchor sites (Bethel Island [BTI] and Sierra Foothill [SNFH]) were added during the 15-day, 5 times/day winter intensive program for both PM_{2.5} and gaseous NH₃ and HNO₃ measurements. The Sacramento/Del Paso (SDP) and San Jose Fourth St. (SJ4) sites also had enhanced measurements. Measurement systems were also enhanced during summer at the Edwards AFB (EDW) site, during fall at the Corcoran Patterson St. (COP) site, and during winter at the Walnut Grove (WAG) tower site.

The satellite network included annual, fall intensive, and winter intensive sampling programs at a total of 53 sites in 8 categories defined by environmental characteristics surrounding the sites (as noted in Table 1.1-1) and included 18 community exposure sites, 11 emissions source dominated sites, 9 visibility sites, 11 intrabasin gradient sites, 2 vertical gradient sites, 1 intrabasin transport site, 6 interbasin transport sites, and 7 boundary/background sites. Detailed site locations, elevations, coordinates are summarized in Table 1.1-2.

The annual satellite network consisted of 14 months of every-sixth-day, 24-hour sampling at 35 PM_{2.5} sites and 7 PM₁₀ sites. The fall intensive study included daily 24-hour sampling of PM₁₀ between 10/09/00 and 11/14/00 at 11 sites. The winter intensive study included daily 24-hour sampling of PM_{2.5} on 13 forecast episode days at 25 sites.

Figure 1.1-1. Maps of monitoring sites in the CRPAQS network (the fall intensive study's 11 PM₁₀ sites are not shown).

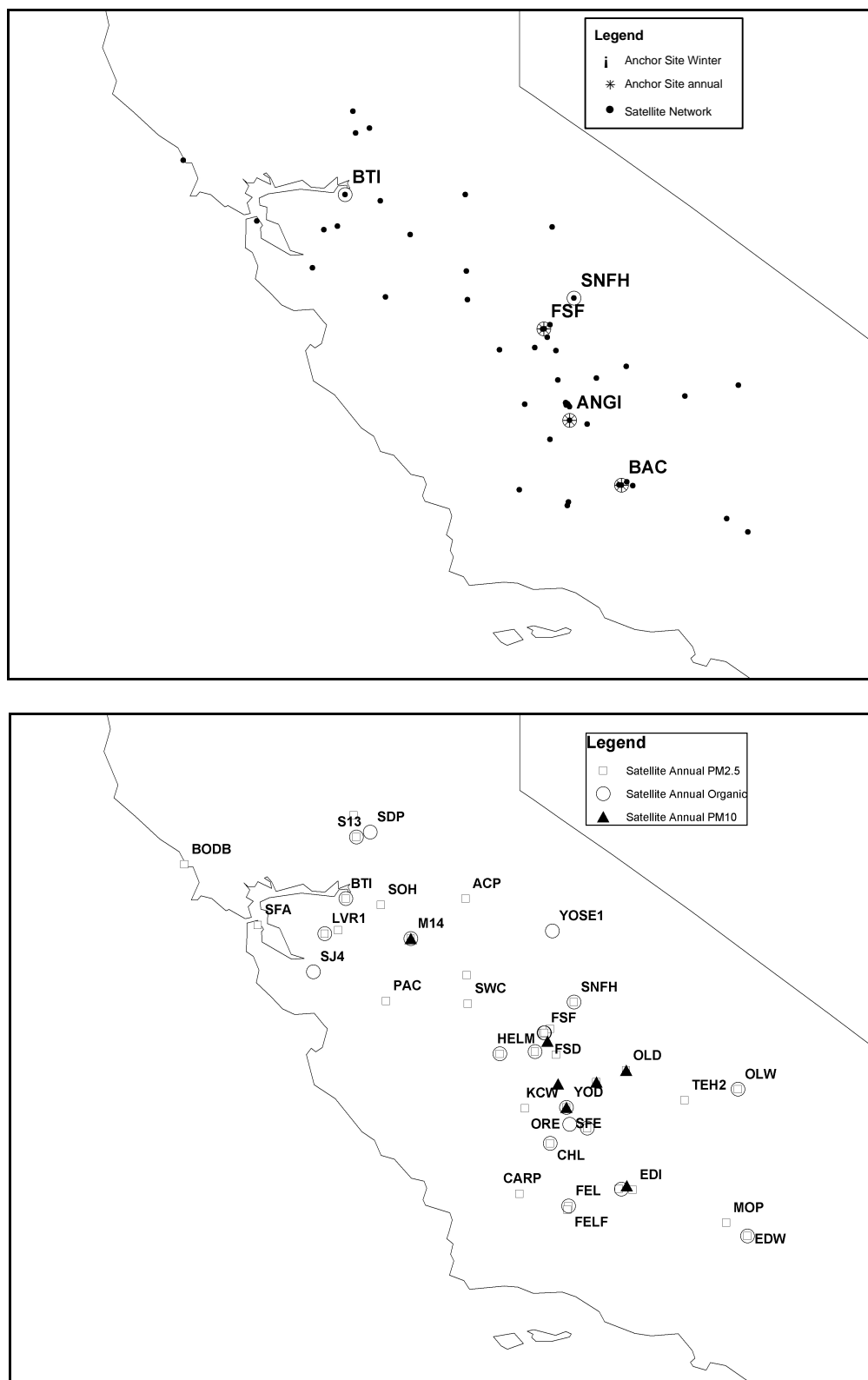


Table 1.1-1. Summary of CRPAQS anchor and satellite site aerosol measurements.^a

			ANCHOR SITES		SATELLITE SITES ^b							
			Sampling Period		Filter Pack					Sampling Period		
Site Code	Site Name	Site Type	Annual ^c	Winter Intensive ^d	PM _{2.5}		PM _{2.5} Organics	PM ₁₀		Annual ^e	Fall Intensive ^f	Winter Intensive ^g
					T/C	q/n	TIGF	T/c	Q/n			
		<i>Minivol module -></i>			<i>A</i> ^h	<i>B</i> ⁱ	<i>D</i> ^j	<i>g</i> ^k	<i>h</i> ^l			
ACP	Angels Camp	Intrabasin Gradient			FTC	FQN				X		X
ALT1	Altamont Pass ^m	Interbasin Transport			FTC					X		X
ANGI	Angiola-ground level	Intrabasin Gradient, Vertical Gradient, Visibility	X	X			TIGF			X		
BAC	Bakersfield-5558 California Street	Community Exposure, Visibility	X	X			TIGF			X		
BGS	Bakersfield-1120 Golden State	Community Exposure						TTC	TQN	(X)		
BODG	Bodega Marine Lab	Boundary/Background			FTC	FQN				X		X
BRES	BAC-Residential	Source- woodburning			FTC	FQN				X		X
BTI	Bethel Island	Interbasin Transport		X	FTC	FQN	TIGF			X		
CARP	Carrizo Plain ^m	Intrabasin Gradient, Visibility			FTC					X		
CHL	China Lake	Visibility			FTC	FQN	TIGF			X		
CLO	Clovis	Community Exposure			FTC	FQN				X		X
CO5	Corcoran Railroad Shoulder	Source - Railroad/ Unpaved Shoulder						TTC			X	
COP	Corcoran-Patterson Avenue	Community Exposure			FTC	FQN	TIGF	TTC	TQN	(X)	X	X
DAIP	Dairy Road - Paved	Source - Paved Road						TTC			X	
DAIU	Dairy Road - Unpaved	Source-Unpaved Road						TTC			X	
EDI	Edison ^m	Intrabasin Gradient			FTC					X		X
EDW	Edwards Air Force Base	Intrabasin Gradient, Visibility			FTC	FQN	TIGF			X		
FEDL	Feedlot or Dairy	Source - Cattle			FTC	FQN	TIGF			X		X
FEL	Fellows	Source- Oilfields			FTC	FQN	TIGF			X		X
FELF	Foothills above Fellows	Intrabasin Gradient			FTC	FQN				X		X
FREM	Fresno MV	Source - Motor Vehicle			FTC	FQN				X		X
FRES	Residential area near FSF, with woodburning	Source - Woodburning			FTC	FQN	TIGF			X		X
FSD	Fresno Drummond	Community Exposure						TTC	TQN	(X)		
FSF	Fresno-3425 First Street	Community Exposure, Visibility	X	X			TIGF			X		
GRA	Grain Elevator	Source - Grain Elevators						TTC	TQN		X	
GRAS	Grain Elevator South	Source - Zone of Influence						TTC	TQN		X	
H43	Highway 43	Southern Boundary						TTC	TQN		X	
HAN	Hanford-Irwin St.	Community Exposure and Fall Northern Boundary						TTC	TQN	(X)	X	
HELM	Agricultural fields/Helm-Central Fresno County	Intrabasin Gradient			FTC	FQN	TIGF			X		X
KCW	Kettleman City ^m	Intrabasin Gradient			FTC					X		X

Table 1.1-1. (continued)

			ANCHOR SITES		SATELLITE SITES ^b							
			Sampling Period		Filter Pack					Sampling Period		
Site Code	Site Name	Site Type	Annual ^c	Winter Intensive ^d	PM _{2.5}		PM _{2.5} Organics	PM ₁₀		Annual ^e	Fall Intensive ^f	Winter Intensive ^g
					T/C	q/n	TIGF	T/c	Q/n			
		<i>Minivol module -></i>			<i>A^h</i>	<i>Bⁱ</i>	<i>D^j</i>	<i>g^k</i>	<i>h^l</i>			
LVR1	Livermore - New site	Interbasin Transport			FTC	FQN	TIGF			X		X
M14	Modesto 14th St.	Community Exposure			FTC	FQN	TIGF	TTC	TQN	(X)		X
MOP	Mojave-Poole	Community Exposure			FTC	FQN				X		
MRM	Merced-midtown	Community Exposure			FTC	FQN				X		X
OLD	Oildale-Manor	Community Exposure			FTC	FQN		TTC	TQN	(X)		
OLW	Olancha	Background			FTC	FQN	TIGF			X		X
ORE	Oregon Avenue	Fall Neighborhood Exposure						TTC			X	
PAC1	Pacheco Pass ^m	Interbasin Transport			FTC					X		
PIXL	Pixley Wildlife Refuge	Rural, Intrabasin Gradient			FTC	FQN	TIGF			X		X
PLE	Pleasant Grove (north of Sacramento)	Intrabasin Gradient			FTC	FQN				X		
S13	Sacramento-1309 T Street	Community Exposure			FTC	FQN	TIGF			X		X
SDP	Sacramento-Del Paso Manor	Community Exposure					TIGF			X		
SELM	Selma(south Fresno area gradient site)	Community Exposure			FTC	FQN				X		X
SFA	San Francisco - Arkansas	Community Exposure			FTC	FQN				X		
SFE	Santa Fe Street	Source - Cotton Handling						TTC	TQN		X	
SJ4	San Jose-4th Street	Community Exposure					TIGF			X		
SNFH	Sierra Nevada Foothills	Vertical Gradient, Intrabasin Gradient, Visibility		X	FTC	FQN	TIGF			X		
SOH	Stockton-Hazelton	Intrabasin Gradient			FTC	FQN				X		X
SWC	SW Chowchilla	Interbasin Transport			FTC	FQN				X		X
TEH2	Tehachapi Pass ^m	Interbasin Transport, Visibility			FTC					X		X
VCS	Visalia Church St.	Community Exposure			FTC	FQN		TTC	TQN	(X)		X
YOD	Yoder Street	Fall Northern Edge of Source Area						TTC			X	
YOSE1	Yosemite National Park-Turtleback Dome	Boundary/Background, Visibility					TIGF			X		
			-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
		Total Number of Sites	3	5	35	29	20	16	11	44	11	25

Table 1.1-1. (continued)

			ANCHOR SITES		SATELLITE SITES ^b							
			Sampling Period		Filter Pack					Sampling Period		
Site Code	Site Name	Site Type	Annual ^c	Winter Intensive ^d	PM _{2.5}		PM _{2.5} Organics	PM ₁₀		Annual ^e	Fall Intensive ^f	Winter Intensive ^g
					T/C	q/n	TIGF	T/c	Q/n			
		<i>Minivol module →</i>			<i>A^h</i>	<i>Bⁱ</i>	<i>D^j</i>	<i>g^k</i>	<i>h^l</i>			
		18	community exposure sites (SDP, S13, SJ4, SFA, MRM, M14, CLO, FSF, SELM, VCS, HAN, COP, FSD, BGS, OLD, BAC, MOP, and ORE)									
		11	emissions source dominated sites (FRES, FREM, FEDL, GRA, GRAS, SFE, BRES, FEL, CO5, DAIP, and DAIU)									
		9	visibility sites (YOSE1, SNFH, FSF, ANGI, CHL, BAC, CARP, TEH2, and EDW)									
		11	intra-basin gradient sites (PLE, ACP, SOH, SNFH, HELM, KCW, ANGI, PIXL, EDI, FELF, and EDW)									
		2	vertical gradient sites (SNFH and ANGI)									
		1	intra-basin transport site (ACP)									
		6	interbasin transport sites (BTI, ALT1, LVR1, PAC1, SWC, and TEH2)									
		7	boundary/background sites (BODG, YOSE1, HAN, OLW, H43, PIXL, and YOD)									

^a Teflon-membrane filter samples were analyzed for mass by gravimetry, filter transmission (b_{abs}) by densitometry, and elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Mo, Pd, Ag, Cd, In, Sn, Sb, Ba, La, Au, Hg, Tl, Pb, and U) by x-ray fluorescence (Watson et al., 1999); quartz-fiber filter samples were analyzed for anions (Cl^- , NO_3^- , SO_4^{2-}) by ion chromatography (Chow and Watson, 1999), ammonium by automated colorimetry, water-soluble Na^+ and K^+ by atomic absorption spectrophotometry, and 7-fraction organic and elemental carbon (OC1 combusted at 120 °C, OC2 at 250 °C, OC3 at 450 °C, OC4 at 550 °C, EC1 at 550 °C, EC2 at 700 °C, and EC3 at 800 °C with pyrolysis correction) by thermal/optical reflectance (Chow et al., 1993b, 2001a); citric-acid-impregnated filter samples were analyzed for ammonia by automated colorimetry; and sodium-chloride-impregnated filters were analyzed for volatilized nitrate by ion chromatography.

^b Sampling with battery-powered Minivol samplers (Airmetrics, Eugene, OR) equipped with $\text{PM}_{10}/\text{PM}_{2.5}$ (in tandem) or PM_{10} inlets at a flow rate of 5 L/min.

^c Anchor site annual sampling program used DRI medium-volume sequential filter samplers (SFS) equipped with Bendix 240 cyclone $\text{PM}_{2.5}$ inlets and preceding anodized aluminum nitric acid denuders. Sampling was conducted daily, 24 hours/day (midnight to midnight) from 12/02/99 to 02/03/01 at a flow rate of 20 L/min. Two filter packs were used for sampling: 1) each Teflon/citric acid filter pack consists of a front Teflon-membrane filter (for mass, b_{abs} , and elemental analyses) backed up by a citric-acid-impregnated cellulose-fiber filter (for ammonia), and 2) each quartz/NaCl filter pack consists of a front quartz-fiber filter (for ion and carbon analyses) backed up by a sodium-chloride-impregnated cellulose-fiber filter (for volatilized nitrate).

^d Anchor site winter intensive sampling included both SFS for $\text{PM}_{2.5}$ sampling and sequential gas samplers (SGS) for ammonia and nitric acid sampling by denuder difference on 15 forecast episode days (12/15/00 to 12/18/00, 12/26/00 to 12/28/00, 01/04/01 to 01/07/01, and 01/31/01 to 02/03/01). The two SGS were equipped with: 1) citric-acid-coated glass denuders and quartz-fiber filters backed up by citric-acid-impregnated cellulose-fiber filters for ammonia (NH_3); and 2) anodized aluminum denuders and quartz-fiber filters backed up by sodium-chloride-impregnated cellulose-fiber filters for nitric acid (HNO_3).

^e The seven PM_{10} sites operated during the annual program are noted with (X). Satellite site annual sampling program included every-sixth-day 24-hour sampling at 35 $\text{PM}_{2.5}$ sites and 7 PM_{10} sites between 12/02/99 and 02/03/01. $\text{PM}_{2.5}$ particulate organic compounds were sampled at 20 sites between 02/06/00 and 01/31/01.

^f Satellite site fall intensive study included 24-hour sampling of PM_{10} on 37 days between 10/09/00 and 11/14/00 at 11 sites. 6 sites (COP, H43, HAN, GRA, GRAS, and SFE) were equipped with both Teflon/citric acid and quartz/NaCl filter packs. 5 sites (CO5, DAIP, DAIU, ORE, and YOD) were equipped with only Teflon/citric acid filter packs.

^g Satellite site winter intensive study included 24-hour sampling of $\text{PM}_{2.5}$ on 13 forecast episode days (12/15/00 to 12/18/00, 12/25/00, 12/27/00, 12/28/00, 01/04/01 to 01/06/01, and 02/01/01 to 02/03/01) at 25 $\text{PM}_{2.5}$ sites, with 21 of the sites equipped with both Teflon/citric acid and quartz/NaCl filter packs.

^h Minivol module A: $\text{PM}_{2.5}$ Teflon/citric acid filter packs at 35 satellite sites. Each filter pack consisted of a front Teflon-membrane filter (for mass, b_{abs} , and elements) backed up by a citric-acid-impregnated cellulose-fiber filter (for ammonia).

Table 1.1-1. (continued)

- ⁱ Minivol module B: PM_{2.5} quartz/NaCl filter packs at 29 satellite sites (same sites as module A but excluding ALT1, PAC1, KCW, EDI, CARP, and TEH2). Each filter pack consisted of a front pre-fired quartz-fiber filter (for ions and carbon) backed up by a sodium-chloride-impregnated cellulose-fiber filter (for volatilized nitrate).
- ^j Minivol module D: PM_{2.5} Teflon-impregnated glass-fiber filters (TIGF) at a total of 20 sites (including 3 annual anchor sites [Fresno, Angiola, and Bakersfield], 14 annual satellite sites, the San Jose-4th St. [SJ4] site, the Sacramento-Del Paso Manor [SPP] site, and the Yosemite [YOSE1] site). A total of 61 samples acquired over the yearlong sampling period were composited as one sample and analyzed by gas chromatography with mass spectrometry (GC/MS) for up to 151 particulate organic compounds as listed in footnote d above.
- ^k Minivol module g: PM₁₀ Teflon/citric acid filter packs at 16 satellite sites, 4 of which (M14, VCS, COP, and OLD) were collocated with annual PM_{2.5} measurements, and 7 of which (M14, VCS, COP, FSD, BGS, HAN, and OLD) were annual PM₁₀ sites. Each filter pack consisted of a front Teflon-membrane filter (for mass, b_{abs}, and elements) backed up by a citric-acid-impregnated cellulose-fiber filter (for ammonia).
- ^l Minivol module h: PM₁₀ quartz/NaCl filter packs at 16 satellite sites, 4 of which were collocated with annual PM_{2.5} measurements (M14, VCS, COP, and OLD), and 7 of which (M14, VCS, COP, FSD, BGS, HAN, and OLD) were annual PM₁₀ sites. Each filter pack consisted of a front quartz-fiber filter (for ion and carbon analyses) backed up by a sodium-chloride-impregnated cellulose-fiber filter (for volatilized nitrate).
- ^m One of six sites (ALT1, PAC1, KCW, EDI, CARP, and TEH2) where only Minivol module A Teflon/citric acid filter packs were acquired.

Table 1.1-2. Site Summary of CRPAQS sampling site locations, elevations, coordinates.

Site Code	Site Address	Elevation (MSL, m) ±1 m or ±5 m*	Coordinates (north) ± 2"	Coordinates (west) ± 2"
ACP	6850 Studhorse Flat Road, Sonora	373*	N 38° 0' 21"	W 120° 29' 29"
ALT1	Flynn Road exit, I-580	350*	N 37° 43' 3"	W 121° 39' 37"
ANGI	36078 4th Avenue, Corcoran	60	N 35° 56' 53"	W 119° 32' 16"
BAC	5558 CA Ave. #430 (STI) #460 (ARB), Bakersfield	119	N 35° 21' 24"	W 119° 3' 45"
BGS	1120 Golden State, Bakersfield	126	N 35° 23' 9"	W 119° 0' 42"
BODG	Bodega Marine Lab, 2099 Westside Road, Bodega Bay	17	N 38° 19' 8"	W 123° 4' 22"
BRES	7301 Remington Avenue, Bakersfield	117	N 35° 21' 29"	W 119° 5' 1"
BTI	5551 Bethel Island Road, Bethel Island	2	N 38° 0' 23"	W 121° 38' 31"
CARP	Soda Springs Road, 0.5 mile south of California Valley	598	N 35° 18' 51"	W 119° 59' 45"
CHL	Baker Site	684	N 35° 46' 27"	W 117° 46' 35"
CLO	908 N. Villa, Clovis	108	N 36° 49' 10"	W 119° 42' 59"
CO5	Pole with transformer on E side of RR tracks, just N of Sherman	64	N 36° 5' 42"	W 119° 33' 15"
COP	1520 Patterson Ave., Corcoran	63	N 36° 6' 8"	W 119° 33' 57"
COP	1520 Patterson Ave., SJVAPCD site	63	N 36° 6' 8"	W 119° 33' 57"
DAIP	Pole #GT209662, 2nd pole S of North Street on Dairy Avenue	63	N 36° 6' 18"	W 119° 34' 19"
DAIU	Pole #CTC1207297, SE corner of Dairy and Tennent	63	N 36° 6' 36"	W 119° 34' 20"
EDI	4101 Kimber Avenue, Bakersfield	118	N 35° 21' 1"	W 118° 57' 26"
EDW	North end of Rawinsonde Road, Edwards AFB	724	N 34° 55' 46"	W 117° 54' 15"
FEDL	8555 S. Valentine, Fresno (near Raisin City)	76	N 36° 36' 40"	W 119° 51' 19"
FEL	Across from 25883 Hwy 33, Fellows	359	N 35° 12' 9"	W 119° 32' 45"
FELF	Texaco Pump Site 47-1, Fellows	512*	N 35° 10' 14"	W 119° 33' 25"
FREM	Pole #16629, 2253 E. Shields Ave., Fresno	96	N 36° 46' 48"	W 119° 47' 0"
FRES	Pole #16962, 3534 Virginia Lane, Fresno	97	N 36° 46' 59"	W 119° 46' 6"
FSD	4706 E. Drummond, Fresno	91	N 36° 42' 20"	W 119° 44' 29"
FSF	3425 First Street, Fresno	97	N 36° 46' 54"	W 119° 46' 24"
GRA	Set of 4 poles just S of Whitley and E of the RR tracks, 30 m W of pole #100	64	N 36° 5' 51"	W 119° 33' 19"
GRAS	Pole #534 on NW corner of Otis and Sherman	64	N 36° 5' 40"	W 119° 33' 17"
H43	Pole at intersection of Hwy 43 and Santa Fe Avenue/4th Avenue, in grassy triangle	64	N 36° 4' 18"	W 119° 32' 10"
HAN	807 S. Irwin St., Hanford	76	N 36° 18' 53"	W 119° 38' 38"

Table 1.1-2. (continued)

Site Code	Site Address	Elevation (MSL, m) ±1 m or ±5 m*	Coordinates (north) ± 2"	Coordinates (west) ± 2"
HELM	Near Placer & Springfield	55	N 36° 35' 26"	W 120° 10' 38"
KCW	Omaha Avenue 2 miles west of Hwy 41, Kettleman City	69	N 36° 5' 41"	W 119° 56' 51"
LVR1	793 Rincon Street, Livermore	138	N 37° 41' 15"	W 121° 47' 3"
M14	814 14th Street, Modesto	28	N 37° 38' 31"	W 120° 59' 40"
MOP	923 Poole Street, Mojave	832	N 35° 3' 2"	W 118° 8' 54"
MRM	2334 M Street, Merced	53	N 37° 18' 30"	W 120° 28' 50"
OLD	3311 Manor Street, Oildale	180	N 35° 26' 17"	W 119° 1' 1"
OLW	Just to east of Hwy 395	1124	N 36° 16' 4"	W 117° 59' 34"
ORE	Cafeteria roof, Mark Twain School, 1500 Oregon Avenue	62	N 36° 5' 15"	W 119° 33' 57"
PAC1	Upper Cottonwood Wildlife Area, west of Los Banos	452*	N 37° 4' 24"	W 121° 13' 18"
PIXL	Road 88, 1.5 miles north of Avenue 56, Alpaugh	69	N 35° 54' 49"	W 119° 22' 33"
PLE	7310 Pacific Avenue, Pleasant Grove	10	N 38° 45' 58"	W 121° 31' 9"
S13	1309 T Street, Sacramento	6	N 38° 34' 6"	W 121° 29' 36"
SDP	2700 Maryal Drive, Sacramento	26	N 38° 36' 49"	W 121° 22' 5"
SELM	7225 Huntsman Avenue, Selma	94	N 36° 34' 58"	W 119° 39' 37"
SFA	10 Arkansas St., San Francisco	6	N 37° 45' 57"	W 122° 23' 56"
SFE	Pole #T207157 on E side of Santa Fe Avenue, 1 mile N of Hwy 43 intersection	64	N 36° 5' 2.3"	W 119° 32' 45"
SJ4	120 N. 4th Street, San Jose	26	N 37° 20' 23"	W 121° 53' 19"
SNFH	31955 Auberry Road, Auberry	589*	N 37° 3' 45"	W 119° 29' 46"
SOH	1601 E. Hazelton, Stockton	8	N 37° 57' 1"	W 121° 16' 8"
SWC	20513 Road 4, Chowchilla	43	N 37° 2' 53"	W 120° 28' 18"
TEH2	Near 19805 Dovetail Court, Tehachapi	1229*	N 35° 10' 4"	W 118° 28' 55"
VCS	310 Church Street, Visalia	102	N 36° 19' 57"	W 119° 17' 28"
YOD	Pole #CTC1039727 on E side of Yoder, just N of Patterson	64	N 36° 6' 6"	W 119° 33' 30"
YOSE1	Turtleback Dome	1685*	N 37° 42' 41"	W 119° 41' 45"

1. All coordinates are referenced to the NAD83 map datum.
2. Coordinates are reported as read by a Garmin GPS device at the site (model GPSII); accuracy is limited to about ±2" (approximately ±50 meters).
3. Elevations are relative to sea level and were determined from a topo map; accuracy is about ±1 meter for valley and coastal sites, ±5 meters for mountain sites (shown with asterisk*).

3.1 Task 1.1.1 – Measurement Equivalence

Several different sampling approaches have been used to acquire mass and chemical composition at the anchor sites. The comparability of these collocated measurements needs to be established to assure the validity of these measurements and to allow the use of some of these methods individually at diverse locations throughout central California to better understand the causes of excessive PM_{2.5}. These collocated measurements include:

- PM_{2.5} mass from Federal Reference Method (FRM) samplers, EPA speciation monitors, DRI sequential filter samplers (SFS), Airmetrics Minivol samplers, micro-orifice uniform deposit impactor (MOUDI) samplers (with PM_{2.5} on the third stage), Met One beta attenuation monitors (BAM), and Rupprecht & Patashnick tapered-element oscillating microbalances (TEOM).
- Collocated continuous nitrate measurements (only at the Fresno site).
- PM₁₀ mass from high-volume, size-selective inlet, BAM, and TEOM.
- PM_{2.5} chemistry from Andersen, MET-ONE, SFS, and Minivol sampler.
- Collocated ammonia from PM_{2.5} and PM₁₀ Minivol samplers (at the Corcoran [COP], Modesto [M14], Oildale [OLD], and Visalia [VCS] sites)
- Filter-based and in-situ continuous nitrate and sulfate monitors.
- Single-wavelength and seven-color aethalometer measurements at 880 nm.
- Filter-based carbon measurements (including OC, EC, and filter transmission [b_{abs}]); thermal evolution carbon analyzer for OC, EC, and TC; and single-wavelength and seven-color aethalometers for BC.
- Collocated light scattering measurements by nephelometer (Fresno only).
- Collocated denuder difference and chemiluminescence nitric acid concentrations (Sierra Foothill, Fresno, and Angiola on 15 episode days).

Field audit results will be reviewed and summarized to determine the accuracy of each measurement (if traceable primary standards are available). Table 1.1-3 summarizes the collocated filter-based PM mass and chemical measurements at CRPAQS and compliance network sites. Table 1.1-4 summarizes the continuous mass and chemical measurements acquired at the anchor sites for comparison. The following definitions will be used to evaluate equivalence, comparability, and predictability (or lack thereof) among different collocated measurements:

Table 1.1-3a. Summary of collocated PM_{2.5} mass and chemical measurements at CRPAQS and compliance network sites.

Site	BAM	TEOM	FRM	Speciation sampler	SFS ^a	Minivol ^a
ANGI-Angiola	X				X	
BAC-Bkf. CA Avenue ^b	X		X	(X)	(X)	
BGS-Bkf. Golden State			X			X
BTI-Bethel Island	X				(X)	(X)
CLO-Clovis, North Villa			X			X
COP-Corcoran, Patterson			X			X
FSF-Fresno 1st Street ^b	X	X	X	(X) (both SASS and RAAS)	(X)	
LVR1-Livermore, Rincon			X			X
M14-Modesto, 14th St.			X			X
MOP-Mojave, Poole St.			X			X
MRM-Merced, Midtown			X			X
S13-Sacramento T St.			X			X
SDP-Sacramento Del Paso ^b			X			X
SFA-San Francisco, Ark.			X			X
SJ4-San Jose 4th Street			X			X
SNFH-Sierra Foothill	X				(X)	(X)
SOH-Stockton, Hazelton			X			X
VCS-Visalia Church St.			X			X

Table 1.1-3b. Summary of collocated PM₁₀ mass measurements at CRPAQS and compliance network sites.^a

Site	BAM	TEOM	Hivol/SSI
BAC-Bkf. CA Avenue ^b	X		X
FSF-Fresno 1st Street ^b	X	X	X

^a Parentheses indicate sites with collocated filter-based measurements (filter transmission [b_{abs}], elements, ions, carbon, and ammonia) and in-situ continuous measurements (nitrate, sulfate, and black carbon from aethalometers; and organic carbon and elemental carbon by thermal evolution methods).

^b Collocated with two FRM samplers at three sites (BAC, FSF, and SDP).

Table 1.1-4. Summary of in-situ continuous measurements acquired at CRPAQS anchor sites.

Site Code	Site Name	PM _{2.5}		PM ₁₀		Particle light scattering (Radiance 903 nephelometer)	PM _{2.5} Organic and elemental carbon (R&P 5400)	PM _{2.5} Particle light absorption (single- and seven-wavelength aethalometers)	PM _{2.5} Nitrate	PM _{2.5} Sulfate
		TEOM	BAM	TEOM	BAM					
ANGI	Angiola		A		A	A ^a	A	A	W ^a	W
BAC	Bakersfield		A		A	A	A	A	W	W
BTI	Bethel Island		W			A		W	W	
COP	Corcoran		F		F	F		F	F	
EDW	Edwards AFB		S		S	A		S		
FSF	Fresno	A	A	A	A	A	A	A	A*	A
SDP	Sacramento–Del Paso Heights		W			A		A		
SJ4	San Jose–4th St.		W			A		A	W	
SNFH	Sierra Foothill		W			A		W	W	
WAG	Walnut Grove					A		W	W ^b	

A = Data available from the annual sampling program between 12/11/99 and 02/03/01.

W = Data available from the winter intensive study period between 12/01/00 and 02/03/01.

F = Data available from the fall intensive study between 10/10/01 and 11/14/01.

* = Collocated measurements at ground level.

^a Measurements at the Angiola site were taken both at ground level and at a location elevated 100 m above ground level.

^b Measurements at the Walnut Grove site were taken both at ground level and at a location elevated 300 m above ground level.

- **Equivalence:** For PM_{2.5} mass concentration, U.S. EPA (1997) requires Federal Equivalent Methods (FEM) to meet the following requirements when collocated with an FRM: 1) collocated precision of 2 µg/m³ or 5% (whichever is larger), 2) linear regression slope of 1 ± 0.05 , 3) linear regression intercept of 0 ± 1 µg/m³, and 4) linear regression correlation coefficient (r) of ≥ 0.97 (U.S. EPA, 1997). Although these criteria are specific to PM_{2.5} mass equivalence, they are also used for PM chemistry equivalence in the analysis to maintain consistency.
- **Comparability:** A comparable monitor should provide readings in units of mass concentration, be equipped with a standardized size-selective inlet, and yield measurements that are the same as collocated sampler measurements. Within stated precision intervals, the criteria for comparability are met when: 1) the slope (by either ordinary least squares [OLS] or effective variance [EF] weighting) equals unity within three standard errors, or average ratios (Y/X) equal unity within one standard deviation, 2) the intercept does not significantly differ from zero within three standard errors, and 3) the correlation coefficient exceeds 0.9 (Berkson, 1950; Kendall, 1951; Madansky, 1959). This is a less demanding definition than equivalence because it considers the reported precisions of the two measurements being compared; these may be larger than that required for a Federal Equivalent Method (FEM) used to determine compliance, but still sufficient to discern concentration differences in space and time.
- **Predictability:** Some measures, such as light absorption, may be correlated with carbon mass concentrations even though they measure different observables in other units. The criterion for predictability between two measurements is met when the correlation coefficient exceeds 0.9, although the slope may substantially deviate from unity and the intercept from zero. Predictability may be qualified, especially when there is high correlation for all but a few outlier measurements. The regression equation is used to estimate carbon concentrations from the measured observable.
- **Non-related:** Measurements are deemed non-related when the correlation coefficient is less than 0.9 and there is no consistent or linear relationship between them.

Comparison statistics are illustrated for four filter-based samplers and three continuous monitors of carbon in Table 1.1-5. Regression slopes and intercepts with ordinary least squares (OLS; Bevington, 1969) and effective variance (EF; Watson et al., 1984) weighting for each pair of measurements, along with their standard errors. OLS does not weight measurements when computing linear regression statistics, whereas EF accounts for measurement uncertainties in both independent and dependent variables to make the data set less likely to be biased by extreme values.

Table 1.1-5 also presents averages of y/x , standard deviations of the average ratios, and the distribution of the data pairs whose difference (y minus x) is less than 1σ , between

Table 1.1-5. Collocated comparison between filter-based and continuous PM_{2.5} measurements acquired between 01/01/00 and 12/26/00 at the Fresno Supersite.

Observable	Sampler ^a	y	x	Effective Variance Weighting ^b		Ordinary Least Squares ^c		Correlation (r)	Number of Pairs	Average Ratio of y/x ± Standard Deviation	Distribution ^d				Average Difference of y - x (µg/m ³)	Precision		
				Regression Slope ± Standard Error	Intercept ± Standard Error	Regression Slope ± Standard Error	Intercept ± Standard Error				del	1σ	2σ	3σ		Collocated	Root Mean Square	P (sig D)
Mass	RAAS	FRM		0.98 ± 0.02	0.92 ± 0.22	0.97 ± 0.01	1.06 ± 0.37	1.00	55	1.07 ± 0.11	28	21	4	2	0.453	2.172	2.510	0.1276
	SFS	FRM		0.77 ± 0.02	1.82 ± 0.19	0.81 ± 0.01	1.37 ± 0.35	1.00	53	0.96 ± 0.17	19	12	9	13	-2.586	5.157	2.210	0.0006
	SFS	RAAS		0.78 ± 0.02	1.15 ± 0.21	0.82 ± 0.01	0.68 ± 0.35	1.00	52	0.89 ± 0.15	16	11	11	14	-3.301	4.990	2.230	0.0000
b_{abs}	RAAS b _{abs}	FRM b _{abs}		0.97 ± 0.03	0.22 ± 0.68	1.03 ± 0.04	-1.24 ± 1.10	0.96	52	0.98 ± 0.15	33	16	1	2	-0.490	4.008	2.710	0.3818
	SFS b _{abs}	FRM b _{abs}		0.95 ± 0.03	-4.62 ± 0.57	1.29 ± 0.09	-10.71 ± 2.66	0.88	55	0.78 ± 0.74	13	3	9	30	-3.794	11.583	1.562	0.0185
	SFS b _{abs}	RAAS b _{abs}		0.98 ± 0.03	-5.81 ± 0.53	1.27 ± 0.09	-10.51 ± 2.49	0.90	54	0.70 ± 0.40	7	10	4	33	-4.096	10.990	1.496	0.0084
TC	RAAS TC	FRM		1.03 ± 0.04	0.05 ± 0.25	1.06 ± 0.02	-0.05 ± 0.25	0.99	53	1.05 ± 0.16	35	13	4	1	0.498	1.325	1.390	0.0085
	RAAS DN TC	FRM		1.01 ± 0.03	-0.97 ± 0.22	1.02 ± 0.02	-0.94 ± 0.28	0.99	53	0.87 ± 0.21	15	23	12	3	-0.718	1.385	1.314	0.0004
	RAAS DN TC	RAAS TC		0.95 ± 0.03	-0.82 ± 0.25	0.96 ± 0.02	-0.84 ± 0.24	0.99	57	0.83 ± 0.19	27	19	8	3	-1.211	1.311	1.410	0.0000
	SFS	RAAS TC		0.84 ± 0.03	0.51 ± 0.22	0.85 ± 0.02	0.49 ± 0.25	0.99	54	0.94 ± 0.19	28	17	8	1	-0.959	1.903	1.440	0.0005
	SFS	FRM		0.91 ± 0.03	0.32 ± 0.19	0.91 ± 0.02	0.41 ± 0.22	0.99	53	0.97 ± 0.14	33	16	3	1	-0.453	1.370	1.320	0.0196
OC	RAAS OC	FRM		1.06 ± 0.04	0.05 ± 0.24	1.08 ± 0.02	0.08 ± 0.24	0.99	53	1.08 ± 0.17	37	9	5	2	0.665	1.277	1.380	0.0004
	RAAS DN OC	FRM		1.00 ± 0.04	-0.67 ± 0.21	0.99 ± 0.02	-0.50 ± 0.25	0.99	53	0.88 ± 0.23	20	20	9	4	-0.601	1.210	1.288	0.0007
	RAAS DN OC	RAAS OC		0.90 ± 0.04	-0.54 ± 0.23	0.91 ± 0.02	-0.54 ± 0.21	0.99	57	0.81 ± 0.20	21	24	7	5	-1.261	1.273	1.390	0.0000
	SFS	FRM		0.93 ± 0.04	0.29 ± 0.18	0.90 ± 0.02	0.49 ± 0.21	0.99	53	0.99 ± 0.13	34	16	2	1	-0.260	1.264	1.230	0.1406
Backup filter OC	RAAS QBK	RAAS OC		0.13 ± 0.02	0.18 ± 0.13	0.13 ± 0.01	0.20 ± 0.10	0.87	55	0.16 ± 0.08	0	1	6	48	-5.990	5.301	1.080	0.0000
	RAAS TBK	RAAS OC		0.06 ± 0.01	1.14 ± 0.07	0.05 ± 0.01	1.22 ± 0.08	0.69	57	0.28 ± 0.13	1	4	3	49	-6.336	7.194	1.110	0.0000
	RAAS QBK	RAAS DNBK		0.57 ± 0.16	0.74 ± 0.12	0.60 ± 0.20	0.75 ± 0.17	0.38	42	2.46 ± 3.43	36	14	2	3	0.505	0.869	0.740	0.0001
	RAAS TBK	RAAS DNBK		0.62 ± 0.12	1.26 ± 0.09	0.58 ± 0.12	1.30 ± 0.10	0.55	44	3.73 ± 3.52	12	23	17	5	1.050	0.550	0.590	0.0000
	RAAS QBK	RAAS TBK		1.12 ± 0.18	-0.69 ± 0.29	1.19 ± 0.14	-0.82 ± 0.24	0.76	55	0.64 ± 0.37	28	25	2	0	-0.509	0.600	0.700	0.0000
EC	RAAS EC	FRM		0.84 ± 0.04	0.06 ± 0.05	0.94 ± 0.03	-0.07 ± 0.10	0.97	53	0.91 ± 0.24	22	25	4	2	-0.202	0.518	0.420	0.0066
	RAAS DN EC	FRM		0.99 ± 0.04	-0.18 ± 0.05	1.10 ± 0.05	-0.31 ± 0.14	0.96	53	0.88 ± 0.24	25	21	7	0	-0.086	0.767	0.482	0.4183
	RAAS DN EC	RAAS EC		0.96 ± 0.07	0.01 ± 0.07	0.98 ± 0.08	0.04 ± 0.12	0.87	52	1.01 ± 0.33	29	16	6	1	0.011	0.465	0.340	0.8699
	SFS	FRM		0.89 ± 0.04	0.01 ± 0.04	0.93 ± 0.02	-0.02 ± 0.08	0.98	53	0.93 ± 0.22	35	11	5	2	-0.163	0.414	0.450	0.0060
TC	R&P5400	FRM		0.43 ± 0.03	5.76 ± 0.17	0.33 ± 0.11	7.89 ± 1.28	0.46	36	1.50 ± 0.67	2	6	6	22	1.844	7.246	1.210	0.1357
	R&P5400	RAAS TC		0.31 ± 0.02	6.22 ± 0.17	0.28 ± 0.10	8.22 ± 1.28	0.42	36	1.48 ± 0.72	4	4	3	25	1.485	7.912	1.340	0.2677
	R&P5400	RAAS DN TC		0.33 ± 0.03	6.42 ± 0.15	0.32 ± 0.11	8.28 ± 1.21	0.45	36	1.83 ± 0.93	2	4	4	26	2.840	7.290	1.260	0.0252
	R&P5400	SFS		0.73 ± 0.04	3.96 ± 0.21	0.60 ± 0.11	5.95 ± 1.38	0.69	37	1.54 ± 0.70	2	2	8	25	2.198	6.799	1.490	0.0569
	R&P5400	PAH		1.40 ± 0.08	6.63 ± 0.08	2.52 ± 0.25	6.22 ± 0.86	0.86	37	19.09 ± 21.67	0	0	0	37	9.442	5.744	1.140	0.0000
OC	R&P5400	FRM		0.02 ± 0.02	6.43 ± 0.10	0.26 ± 0.11	6.82 ± 0.98	0.38	36	1.56 ± 0.70	0	7	5	24	1.629	5.762	0.970	0.0987
	R&P5400	RAAS OC		0.20 ± 0.02	5.42 ± 0.11	0.19 ± 0.10	7.20 ± 0.98	0.31	36	1.48 ± 0.73	3	4	5	24	1.010	6.747	1.140	0.3751
	R&P5400	RAAS DN OC		0.24 ± 0.02	5.53 ± 0.10	0.24 ± 0.11	7.09 ± 0.92	0.37	36	1.89 ± 0.99	2	3	4	27	2.296	5.995	1.040	0.0277
	R&P5400	SFS		0.78 ± 0.04	3.41 ± 0.18	0.48 ± 0.10	5.44 ± 0.99	0.64	37	1.55 ± 0.70	1	2	8	26	1.609	5.445	1.140	0.0806
	R&P5400	PAH		0.80 ± 0.05	5.10 ± 0.06	1.57 ± 0.20	5.67 ± 0.67	0.80	37	16.60 ± 20.44	0	0	0	37	6.886	3.507	0.790	0.0000

Table 1.1-5. (continued)

Observable	Sampler ^a		Effective Variance Weighting ^b		Ordinary Least Squares ^c		Correlation (r)	Number of Pairs	Average Ratio of y/x ± Standard Deviation	Distribution ^d				Average Difference of y - x (µg/m ³)	Precision		
	y	x	Regression Slope ± Standard Error	Intercept ± Standard Error	Regression Slope ± Standard Error	Intercept ± Standard Error				del	1σ	2σ	3σ		Collocated	Root Mean Square	P (sig D)
EC	R&P5400	FRM	1.06 ± 0.06	0.09 ± 0.07	1.30 ± 0.30	0.07 ± 0.57	0.61	33	1.38 ± 1.27	14	7	2	10	0.557	1.638	0.380	0.0596
	R&P5400	RAAS EC	1.10 ± 0.09	0.23 ± 0.10	1.75 ± 0.28	-0.34 ± 0.46	0.74	34	1.53 ± 1.23	8	9	5	12	0.701	1.516	0.390	0.0109
	R&P5400	RAAS DN EC	0.80 ± 0.06	0.56 ± 0.06	0.59 ± 0.17	1.21 ± 0.42	0.50	36	1.52 ± 1.33	8	8	7	13	0.520	1.909	0.480	0.1112
	R&P5400	SFS	0.90 ± 0.07	0.32 ± 0.07	1.05 ± 0.30	0.43 ± 0.47	0.53	32	1.44 ± 1.05	5	11	7	9	0.497	1.295	0.360	0.0377
	R&P5400	PAH	0.65 ± 0.03	0.82 ± 0.03	0.95 ± 0.10	0.55 ± 0.33	0.86	37	2.48 ± 3.62	5	8	8	16	0.434	1.549	0.500	0.0971
	R&P5400	AETH1	1.05 ± 0.05	0.28 ± 0.05	1.32 ± 0.22	0.44 ± 0.50	0.71	37	1.63 ± 1.11	7	5	8	17	0.944	2.166	0.470	0.0118
EC	R&P5400	AETH7	1.43 ± 0.07	0.05 ± 0.06	2.87 ± 0.23	-1.07 ± 0.34	0.90	38	1.77 ± 1.17	6	3	5	24	1.179	2.124	0.440	0.0015
	FRM b _{abs}	FRM EC	11.58 ± 0.50	2.82 ± 0.63	11.35 ± 0.75	3.63 ± 1.35	0.91	50	14.50 ± 3.84	1	0	0	49	19.547	11.108	2.110	0
	RAAS b _{abs}	RAAS EC	11.36 ± 0.58	5.19 ± 0.70	11.92 ± 0.72	4.59 ± 1.13	0.92	52	16.84 ± 4.78	0	0	0	52	19.011	10.269	1.530	0
	RAAS b _{abs}	RAAS DN EC	7.60 ± 0.29	8.51 ± 0.40	5.79 ± 0.40	12.31 ± 1.25	0.89	57	17.16 ± 7.19	0	0	0	57	21.857	13.673	1.770	0
	SFS b _{abs}	SFS EC	10.22 ± 0.39	-0.62 ± 0.47	9.33 ± 0.56	1.18 ± 1.68	0.91	58	9.73 ± 4.99	4	2	2	50	18.082	21.128	2.774	0
	FRM EC	FRM b _{abs}	0.07 ± 0.00	0.05 ± 0.05	0.07 ± 0.01	0.00 ± 0.12	0.91	50	0.08 ± 0.07	1	0	0	49	-19.547	11.108	2.110	0
	RAAS EC	RAAS b _{abs}	0.07 ± 0.00	-0.08 ± 0.07	0.07 ± 0.00	-0.12 ± 0.10	0.92	52	0.06 ± 0.02	0	0	0	52	-19.011	10.269	1.530	0
	RAAS DN EC	RAAS b _{abs}	0.09 ± 0.00	-0.47 ± 0.07	0.14 ± 0.01	-1.26 ± 0.27	0.89	57	0.07 ± 0.03	0	0	0	57	-21.857	13.673	1.770	0
	SFS EC	SFS b _{abs}	0.06 ± 0.00	0.36 ± 0.03	0.09 ± 0.01	0.23 ± 0.16	0.91	53	0.11 ± 0.05	4	2	2	50	-18.082	21.128	2.774	0
BC/EC	AETH1	FRM	0.77 ± 0.02	0.05 ± 0.03	0.79 ± 0.03	-0.02 ± 0.09	0.97	50	0.79 ± 0.19	16	11	11	12	-0.473	0.621	0.360	0.0000
	AETH7	FRM	0.71 ± 0.03	0.05 ± 0.02	0.60 ± 0.04	0.17 ± 0.08	0.90	50	0.75 ± 0.21	11	12	10	17	-0.432	0.475	0.250	0.0000
	AETH1	RAAS EC	0.81 ± 0.03	0.13 ± 0.04	0.83 ± 0.02	0.09 ± 0.06	0.98	51	0.92 ± 0.25	23	23	3	2	-0.250	0.490	0.380	0.0006
	AETH7	RAAS EC	0.63 ± 0.03	0.24 ± 0.04	0.66 ± 0.05	0.22 ± 0.07	0.89	51	0.89 ± 0.29	21	14	11	5	-0.238	0.412	0.270	0.0001
	AETH1	RAAS DN EC	0.72 ± 0.03	0.22 ± 0.03	0.69 ± 0.02	0.26 ± 0.07	0.98	51	0.93 ± 0.26	21	24	4	2	-0.387	0.875	0.440	0.0027
	AETH7	RAAS DN EC	0.64 ± 0.03	0.24 ± 0.03	0.60 ± 0.04	0.28 ± 0.06	0.91	51	0.93 ± 0.30	27	16	6	2	-0.254	0.468	0.330	0.0003
	AETH1	SFS	0.82 ± 0.03	0.08 ± 0.03	0.78 ± 0.03	0.12 ± 0.09	0.97	52	0.87 ± 0.21	23	22	6	1	-0.355	0.696	0.450	0.0006
	AETH7	SFS	0.74 ± 0.03	0.09 ± 0.03	0.57 ± 0.03	0.29 ± 0.06	0.93	52	0.83 ± 0.24	22	18	8	4	-0.352	0.715	0.340	0.0008
	AETH7	AETH1	0.89 ± 0.02	0.04 ± 0.02	0.86 ± 0.01	0.07 ± 0.02	1.00	50	0.94 ± 0.11	35	13	2	0	-0.107	0.159	0.270	0.0000
TC	PAH	FRM	0.15 ± 0.01	-0.37 ± 0.03	0.15 ± 0.02	0.15 ± 0.27	0.74	52	0.15 ± 0.14	0	0	0	52	-8.107	8.063	0.920	0.0000
	PAH	RAAS TC	0.13 ± 0.01	-0.29 ± 0.03	0.14 ± 0.02	0.21 ± 0.27	0.72	53	0.15 ± 0.14	0	0	2	51	-8.591	8.643	1.090	0.0000
	PAH	RAAS DN TC	0.11 ± 0.00	-0.13 ± 0.02	0.14 ± 0.02	0.34 ± 0.25	0.72	53	0.19 ± 0.17	0	2	1	50	-7.354	8.367	0.990	0.0000
	PAH	SFS	0.16 ± 0.01	-0.38 ± 0.03	0.20 ± 0.02	-0.10 ± 0.29	0.79	54	0.17 ± 0.16	0	0	0	54	-7.723	7.760	1.060	0.0000
	PAH	R&P5400	0.03 ± 0.00	-0.01 ± 0.02	0.29 ± 0.03	-1.27 ± 0.41	0.86	37	0.15 ± 0.13	0	0	0	37	-9.442	5.744	1.140	0.0000
OC	PAH	FRM	0.20 ± 0.01	-0.45 ± 0.03	0.20 ± 0.03	0.15 ± 0.27	0.73	52	0.20 ± 0.19	0	0	2	50	-5.945	5.975	0.910	0.0000
	PAH	RAAS OC	0.15 ± 0.01	-0.27 ± 0.04	0.17 ± 0.02	0.20 ± 0.27	0.71	53	0.19 ± 0.18	0	0	3	50	-6.615	6.614	1.090	0.0000
	PAH	RAAS DN OC	0.13 ± 0.01	-0.11 ± 0.03	0.19 ± 0.03	0.30 ± 0.25	0.72	53	0.25 ± 0.23	1	6	2	44	-5.312	5.983	0.970	0.0000
	PAH	SFS	0.22 ± 0.01	-0.48 ± 0.04	0.26 ± 0.03	-0.15 ± 0.30	0.79	54	0.22 ± 0.21	0	1	3	50	-5.661	5.554	0.930	0.0000
	PAH	R&P5400	0.00 ± 0.00	0.22 ± 0.01	0.41 ± 0.05	-1.57 ± 0.54	0.80	37	0.21 ± 0.18	0	0	0	37	-6.886	3.507	0.790	0.0000

Table 1.1-5. (continued)

Observable	Sampler ^a		Effective Variance Weighting ^b		Ordinary Least Squares ^c		Correlation (r)	Number of Pairs	Average Ratio of y/x ± Standard Deviation	Distribution ^d				Average Difference of y - x (µg/m ³)	Precision		
	y	x	Regression Slope ± Standard Error	Intercept ± Standard Error	Regression Slope ± Standard Error	Intercept ± Standard Error				del	1σ	2σ	3σ		Collocated	Root Mean Square	P (sig D)
EC	PAH	FRM	0.64 ± 0.03	-0.22 ± 0.03	1.43 ± 0.17	-0.85 ± 0.31	0.79	46	0.71 ± 0.61	0	7	3	36	-0.182	1.181	0.280	0.3009
	PAH	RAAS EC	1.17 ± 0.07	-0.55 ± 0.07	1.60 ± 0.17	-0.84 ± 0.27	0.82	48	0.82 ± 0.69	5	11	4	28	-0.031	1.115	0.290	0.8465
	PAH	RAAS DN EC	0.57 ± 0.02	0.01 ± 0.03	0.52 ± 0.08	0.54 ± 0.25	0.68	53	0.83 ± 0.73	6	8	16	23	-0.463	1.834	0.440	0.0717
	PAH	SFS	0.57 ± 0.03	-0.10 ± 0.03	1.30 ± 0.20	-0.49 ± 0.31	0.70	46	0.79 ± 0.69	5	5	6	30	-0.100	1.131	0.280	0.5499
	PAH	R&P5400	0.47 ± 0.02	-0.14 ± 0.03	0.77 ± 0.08	0.14 ± 0.31	0.86	34	0.73 ± 0.49	5	8	8	16	-0.434	1.549	0.500	0.0971
	PAH	AETH1	0.53 ± 0.02	-0.12 ± 0.01	0.96 ± 0.13	0.11 ± 0.33	0.73	52	0.92 ± 0.86	8	2	4	38	0.033	1.695	0.330	0.8887
	PAH	AETH7	0.37 ± 0.01	0.00 ± 0.01	2.18 ± 0.20	-0.98 ± 0.29	0.84	52	1.05 ± 0.96	10	1	0	41	0.389	1.644	0.310	0.0940

^a AETH1 = Single-wavelength aethalometer (Magee Scientific, Berkeley, CA), µg/m³.
AETH7 = Seven-color aethalometer (Andersen Instruments, Smyrna, GA), µg/m³.
FRM = Single-channel Federal Reference Method sampler (Andersen Instruments, Smyrna, GA), µg/m³.
PAH = PAS 2000 Real-Time PAH Monitor (EcoChem Analytics, West Hills, CA), relative units.
QBK = Quartz backup filter carbon from the RAAS non-denuded quartz/quartz channel, µg/m³.
R&P5400 = Ambient Particulate Carbon Monitor Model 5400 (Rupprecht & Patashnick, Albany, NY), µg/m³.
RAAS = Reference Ambient Aerosol Sampler (Andersen Instruments, Smyrna, GA), µg/m³.
RAAS DN = Quartz front filter carbon from the RAAS denuded quartz/quartz channel, µg/m³.
RAAS DNBK = Quartz backup filter carbon from the RAAS denuded quartz/quartz channel, µg/m³.
RAAS TC, OC, and EC = Quartz front filter TC, OC, and EC from the RAAS non-denuded quartz/quartz channel, µg/m³.
SFS = Sequential Filter Sampler (Desert Research Institute, Reno, NV), µg/m³.
TBK = Quartz backup filter carbon from the RAAS non-denuded Teflon/quartz channel, µg/m³.
FRM _{b_{abs}} = Light absorption from FRM Teflon filter, Mm⁻¹.
RAAS _{b_{abs}} = Light absorption from RAAS Teflon filter, Mm⁻¹.
SFS _{b_{abs}} = Light absorption from SFS Teflon filter, Mm⁻¹.

^b Effective variance least squares (Watson et al., 1984) weights variable by precisions in both variables.

^c Ordinary least squares does not weight variables by their precisions (Bevington, 1969).

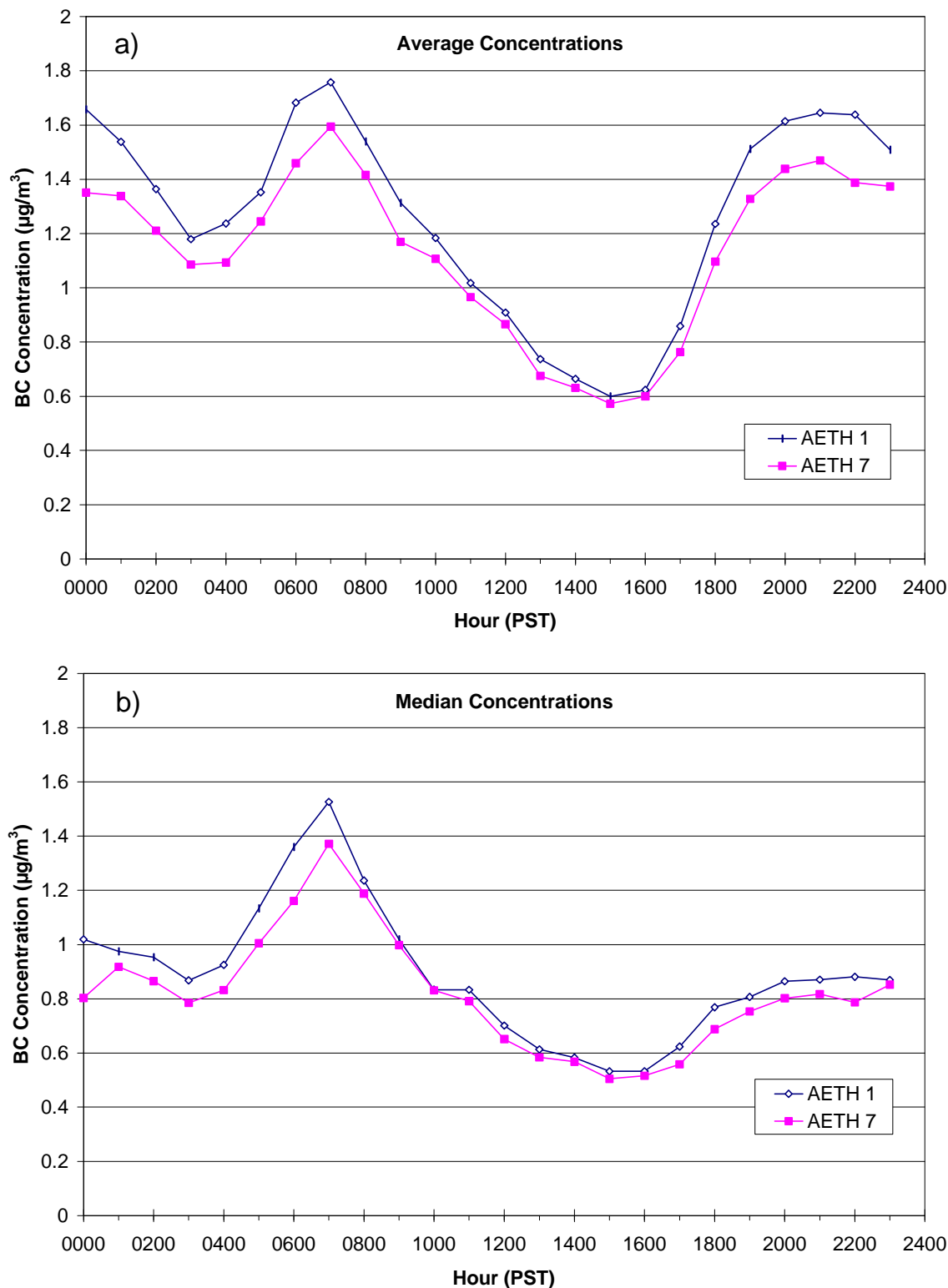
^d Number of sample concentration differences between stated precision intervals (s) for the difference.

1 and 2σ , between 2 and 3σ , and greater than 3σ . Here, σ is the measurement uncertainty of $y - x$, which is the square root of the sum of the squared uncertainties ($\sigma_x^2 + \sigma_y^2$), where σ_x and σ_y are the one standard deviation precisions for the x and y observables, respectively. Measurement precisions were estimated from replicate analyses of samples collected by that sampler. Table 1.1-5 gives the average of the paired differences ($y - x$) between the x and y sampler; the collocated precision, which is the standard deviation of the paired differences; and the root mean squared (RMS) precision (the square root of the mean squared precisions), which is essentially the average measurement uncertainty of " $y - x$." The average differences and collocated precisions can be used to test the statistical hypothesis that the difference between samplers x and y is zero. A parametric test (Student's t-test) is performed for each pair of samplers. The probability (P) for a greater absolute value of student's t-statistic is also given in Table 1.1-5. If P is less than 0.05, one can infer that one of the measurements is significantly larger or smaller than the other measurement, depending on the sign of the average difference.

Table 1.1-5 shows that 880-nm black carbon measurements (BC) from the two aethalometers are highly correlated ($r = 1$) with low intercepts (0.04 to 0.07 $\mu\text{g}/\text{m}^3$) for measurements taken at the Fresno site. The two aethalometers meet the criteria for comparability, but not for equivalence. AETH7 reports an average of 0.11 $\mu\text{g}/\text{m}^3$ (~9%) less BC than AETH1. Figure 1.1-2 shows that hourly average BC levels peak around 0600 to 0700 PST and again around 2000 to midnight PST, with a small dip at 2300 PST. This is consistent with increased morning and evening traffic emissions from nearby roadways. Emissions from residential wood combustion during winter may also contribute to the prolonged peak during late evening. The peaks and valleys of the two aethalometers track each other closely, with the lowest differences (0.02 to 0.06 $\mu\text{g}/\text{m}^3$ BC) found between 1100 and 1600 PST. Morning measurements at Fresno are affected by shallow surface radiation inversions formed overnight that typically couple with the valleywide mixed layer around 1000 to 1100 PST and dilute primary BC emissions; afternoons are affected by increased ventilation. The largest differences between the two aethalometers ($>0.20 \mu\text{g}/\text{m}^3$) occurs around midnight, 0100, 0600, and 2200 PST when the black carbon concentrations are highest.

Only the morning peak (0600 to 0700 PST) is found for the hourly median BC in Figure 1.1-2b, indicating that the afternoon averages are affected by a few large concentrations. Evening peaks occur on cold winter nights when hourly black carbon levels exceed 80 $\mu\text{g}/\text{m}^3$. Median concentrations during the morning peak are ~0.23 $\mu\text{g}/\text{m}^3$ lower than the corresponding average concentrations. Differences between hourly median single-wavelength vs. seven-color aethalometer BC concentrations are less than 0.04 $\mu\text{g}/\text{m}^3$ from 0900 to 1600 PST, but exceed 0.15 $\mu\text{g}/\text{m}^3$ at midnight, 0600, and 0700 PST. An examination of 5-minute data shows that an apparent jump (~10-25%) occurs when the filter tape advances from one sample spot to the next. The filter tape in the seven-color aethalometer advances about twice as often as the single-wavelength aethalometer tape, resulting in more data loss (10- to 20-minute data losses per tape advance). This might be a cause of the discrepancies between the two instruments, higher concentrations during the evening and morning hours result in more frequent tape advances.

Figure 1.1-2. Diurnal variations of hourly black carbon concentrations from the single-wavelength (AETH1) and seven-color (AETH7) aethalometers for: a) average concentrations, and b) median concentrations, measured at 880 nm for every-sixth-day samples acquired at the Fresno Supersite during 2000.



This type of pairwise comparison will be made and interpreted for all collocated measurements to establish the equivalence, comparability, and predictability between measurements from different instruments.

3.2 Task 1.1.2 – Accuracy, Precision, and Validity of the Optical Measurements

Collocated particle light scattering from Radiance Research M903 nephelometers prior to field deployment and the five nephelometers (Radiance Research M903 at 530 nm with and without preceding PM_{2.5} inlet, Optec NGN-2 ambient temperature nephelometer, Greentek GT640 photometer at 780 nm, and TSI DusTrak 8520 photometer at 780 nm) at the Fresno site will be compared as part of Task 1.1.1 to determine measurement precision, validity, and bias. Audit data will also be used to evaluate accuracy.

Particle light scattering (measured by nephelometer) and particle light absorption (measured by aethalometer) can be evaluated by establishing the relationship between PM filter measurements and optical measurements. The following comparisons will be made to evaluate:

- Relationships between particle light scattering and PM_{2.5} mass; and
- Relationships between particle light absorption by single- or seven-color aethalometers and filter transmission (b_{abs}), organic and elemental carbon by thermal/optical reflectance, and elemental carbon from in-situ continuous thermal evolution methods.

3.2.1 Relationship between PM_{2.5} Mass and Light Scattering

Particle light scattering (b_{sp}) may be a cost-effective surrogate for PM_{2.5} concentrations at community-representative sites (Watson et al., 1998a). Because b_{sp} can be accurately measured on time scales as short as one minute, it could be useful for evaluating short-term temporal variations of PM_{2.5}. Light scattering has been related to TSP, PM₁₀, and PM_{2.5} mass and chemical component concentrations in urban, non-urban, and background areas (e.g., Charlson et al., 1968; Horvath and Noll, 1969; Garland and Rae, 1970; Harrison, 1979; Johnson, 1981; Malm et al., 1981; Heintzenberg and Bäcklin, 1983; Gordon and Johnson, 1985; Ruby, 1985; Ruby et al., 1989; Mulholland and Bryner, 1994; White et al., 1994; Leong et al., 1995; Heintzenberg and Charlson, 1996; Watson et al., 1996; Kerker, 1997; Molenaar, 1997). Although light scattering is often highly correlated with mass concentrations, the relationship is not necessarily unique and may be different from location to location and for different seasons of the year.

The amount of light scattered per unit particle mass concentration ($\mu\text{g}/\text{m}^3$) is commonly referred to as the mass scattering efficiency in units of m^2/g . Mass scattering efficiency is not well defined (White, 1986; White et al., 1994) as it depends on particle size, shape, and refractive index that may vary in time and space. Nonetheless, relationships among size-resolved mass concentration and light scattering from most past studies are consistent. Chow et al. (2001b) summarized mass scattering efficiencies from 10 sites and found that PM_{2.5} mass scattering efficiencies were about $2 \text{ m}^2/\text{g}$. Although PM_{2.5} particle

scattering efficiencies may vary temporally and geographically, continuous light scattering measurements may be useful as an indicator of short-term variations in PM_{2.5} mass concentrations. For such relationships to be useful, they must be made using consistent methodology. Nephelometer measurements should be made on the fine particle size fraction under dry conditions.

Nineteen of the annual sites, 9 of the fall intensive sites, and 23 of the winter sites listed in Table 1.1-6 included collocated Radiance Research M903 nephelometers with either Airmetrics Minivol samplers or sequential filter samplers. The nephelometers measured total particle scattering (except at Fresno where both fine and total particle light scattering measurements were acquired) and were equipped with “smart” heaters that only operated when relative humidity (RH) exceeded 65%. Relationships between PM_{2.5} mass concentrations and particle light scattering will be determined, compared, and evaluated to assess how well total particle scattering might represent PM_{2.5} mass concentrations measured gravimetrically from filter samples. Differences between fine and total particle light scattering will be examined to determine whether fine particle scattering (rather than total particle scattering) is a better surrogate for PM_{2.5} mass.

In this analysis, particle mass and light scattering will be compared using linear regression of b_{sp} on PM_{2.5} and PM_{2.5} on b_{sp} , resulting in a mass scattering efficiency and a predictor for PM_{2.5} mass concentration, respectively. Figure 1.1-3 shows an example from two sites that have been used to estimate the regional, urban, and neighborhood contributions to PM_{2.5} at Fresno. Average and median ratios of $b_{sp}/PM_{2.5}$ and $PM_{2.5}/b_{sp}$ will also be calculated. If necessary, data points with lower RH limits will be extracted to further minimize the effects of RH on particle scattering.

The resulting regression statistics will be examined for differences due to site type (based on the eight site categories defined in Table 1.1-1), sampling location/elevation, sampling period, meteorology (wind speed, wind direction, temperature, and relative humidity), and ambient PM_{2.5} levels to determine when and where particle light scattering measurements can be used as a surrogate for PM measurements.

3.2.2 Relationship between Continuous and Filter-Based Particle Light Absorption Measurements

Table 1.1-5 presents a cross-comparison between filter light transmission (b_{abs}) and elemental carbon (EC), Rupprecht & Patashnick 5400 EC, and aethalometer black carbon (BC). The following subsections describe the relationships between filter b_{abs} and EC and compare filter-based measurements with aethalometer measurements.

3.2.2.a b_{abs} vs. EC Measurements on Filters

The relationship between b_{abs} by densitometry on the Teflon-membrane filter and EC measurements by thermal/optical reflectance (TOR) on quartz-fiber filters can be derived. Outliers can be identified from scatter plots and regression statistics. The regression coefficient (absorption coefficient in m²/g) can be used to estimate BC concentrations for

Table 1.1-6. Summary of PM_{2.5}, PM₁₀, and nephelometer measurements in the CRPAQS anchor and satellite network.^a

Site Code	Site Name	Site Type	PM _{2.5} /PM ₁₀ Filter Pack				PM _{2.5} /PM ₁₀ Sampling Period			Nephelometer Sampling Period			
			PM _{2.5}		PM ₁₀		Annual ^b	Fall Intensive ^c	Winter Intensive ^d	Annual ^b	Fall Intensive ^c	Winter Intensive ^d	Summer
			T/C	q/n	T/c	Q/n							
		<i>Minivol module -></i>	A ^e	B ^f	g ^g	h ^h							
ACP	Angels Camp	Intrabasin Gradient	FTC	FQN			X		X			X	
ALT1 ⁱ	Altamont Pass	Interbasin Transport	FTC				X		X			X	
ANG1 ⁱ	Angiola-ground level	Intrabasin Gradient, Vertical Gradient, Visibility					X						
BAC ^j	Bakersfield-5558 California Street	Community Exposure, Visibility					X						
BARS	Barstow	Visibility								X			
BEL	Corcoran-Bell St.	Community Exposure									X		
BGS	Bakersfield-1120 Golden State	Community Exposure			TTC	TQN	(X)						
BODG	Bodega Marine Lab	Boundary/Background	FTC	FQN			X		X	X		X	
BQUC	Bouquet Canyon station	Interbasin Transport, Visibility											X
BRES	BAC-Residential	Source- woodburning	FTC	FQN			X		X			X	
BTI	Bethel Island	Interbasin Transport	FTC	FQN			X			X			
CAJP	Cajon Pass station	Interbasin Transport, Visibility											X
CANL	Canal station	Intrabasin Gradient, Visibility									X		
CANT	Cantil station	Intrabasin Gradient, Visibility											X
CARP ^j	Carrizo Plain	Intrabasin Gradient, Visibility	FTC				X			X			
CHL	China Lake	Visibility	FTC	FQN			X			X			
CLO	Clovis	Community Exposure	FTC	FQN			X		X			X	
CO5	Corcoran Railroad Shoulder	Source - Railroad/ Unpaved Shoulder			TTC			X					
COP	Corcoran-Patterson Avenue	Community Exposure	FTC	FQN	TTC	TQN	(X)	X	X			X	
COPE	Corcoran-Focus East station	Source - Zone of Influence									X		
COPN	Corcoran-Focus North station	Source - Zone of Influence									X		
COPS	Corcoran-Focus South station	Source - Zone of Influence									X		
COPW	Corcoran-Focus West station	Source - Zone of Influence									X		
COV	Corcoran-1000 Van Dorsten station	Source - Zone of Influence									X		
CRLD	Crows Landing (Patterson) station	Intrabasin Gradient								X			
DAIP	Dairy Road - Paved	Source - Paved Road			TTC			X			X		
DAIU	Dairy Road - Unpaved	Source-Unpaved Road			TTC			X			X		
DUB1	Dublin station	Intrabasin Gradient								X			
EDF ^j	Edison	Intrabasin Gradient	FTC				X		X			X	
EDW	Edwards Air Force Base	Intrabasin Gradient, Visibility	FTC	FQN			X			X			
FEDL	Feedlot or Dairy	Source - Cattle	FTC	FQN			X		X	X		X	
FEL	Fellows	Source- Oilfields	FTC	FQN			X		X	X		X	
FELF	Foothills above Fellows	Intrabasin Gradient	FTC	FQN			X		X	X		X	
FREM	Fresno MV	Source - Motor Vehicle	FTC	FQN			X		X	X		X	
FRES	Residential area near FSF, with woodburning	Source - Woodburning	FTC	FQN			X		X	X		X	

Table 1.1-6. (continued)

Site Code	Site Name	Site Type	PM _{2.5} /PM ₁₀ Filter Pack				PM _{2.5} /PM ₁₀ Sampling Period			Nephelometer Sampling Period			
			PM _{2.5}		PM ₁₀		Annual ^e	Fall Intensive ^f	Winter Intensive ^g	Annual ^e	Fall Intensive ^f	Winter Intensive ^g	Summer
			T/C	q/n	T/c	Q/n							
		<i>Minivol module -></i>	A ^h	B ⁱ	g ^k	h ^l							
FSD	Fresno Drummond	Community Exposure			TTC	TQN	(X)						
FSF ^l	Fresno-3425 First Street	Community Exposure, Visibility					X						
GRA	Grain Elevator	Source - Grain Elevators			TTC	TQN		X			X		
GRAE	Grain Elevator East	Source - Zone of Influence									X		
GRAN	Grain Elevator North	Source - Zone of Influence									X		
GRAS	Grain Elevator South	Source - Zone of Influence			TTC	TQN		X			X		
GRAW	Grain Elevator West	Source - Zone of Influence									X		
H43	Highway 43	Southern Boundary			TTC	TQN		X			X		
HAN	Hanford-Irwin St.	Community Exposure and Fall Northern Boundary			TTC	TQN	(X)	X				X	
HELM	Agricultural fields/Helm-Central Fresno County	Intrabasin Gradient	FTC	FQN			X		X			X	
KCW ^l	Kettleman City	Intrabasin Gradient	FTC				X		X			X	
KRV	Trimmer (Kings River Valley) station	Interbasin Transport								X			
LATN	Laten station	Intrabasin Gradient, Visibility									X		
LVR1	Livermore - New site	Interbasin Transport	FTC	FQN			X		X			X	
M14	Modesto 14th St.	Community Exposure	FTC	FQN	TTC	TQN	(X)		X				
MOP	Mojave-Poole	Community Exposure	FTC	FQN			X						
MRM	Merced-midtown	Community Exposure	FTC	FQN			X		X			X	
NIL	Corcoran-Niles St. station	Background									X		
OLD	Oildale-Manor	Community Exposure	FTC	FQN	TTC	TQN	(X)					X	
OLW	Olancho	Background	FTC	FQN			X		X	X		X	
ORE	Oregon Avenue	Fall Neighborhood Exposure			TTC			X					
OTT	Corcoran-Ottawa station (south Corcoran)	Source - Zone of Influence									X		
PAC1 ^l	Pacheco Pass	Interbasin Transport	FTC				X			X			
PIXL	Pixley Wildlife Refuge	Rural, Intrabasin Gradient	FTC	FQN			X		X	X		X	
PLE	Pleasant Grove (north of Sacramento)	Intrabasin Gradient	FTC	FQN			X					X	
S13	Sacramento-1309 T Street	Community Exposure	FTC	FQN			X		X			X	
SDP	Sacramento-Del Paso Manor	Community Exposure								X			
SELM	Selma(south Fresno area gradient site)	Community Exposure	FTC	FQN			X		X	X		X	
SFA	San Francisco - Arkansas	Community Exposure	FTC	FQN			X					X	
SFE	Santa Fe Street	Source - Cotton Handling			TTC	TQN		X			X		
SHE	Corcoran-Sherman St. station	Community Exposure									X		
SJ4	San Jose-4th Street	Community Exposure											
SLDC	Soledad Canyon station	Interbasin Transport, Visibility											X
SNFH	Sierra Nevada Foothills	Vertical Gradient, Intrabasin Gradient, Visibility	FTC	FQN			X			X			
SOH	Stockton-Hazelton	Intrabasin Gradient	FTC	FQN			X		X				

Table 1.1-6. (continued)

Site Code	Site Name	Site Type	PM _{2.5} /PM ₁₀ Filter Pack				PM _{2.5} /PM ₁₀ Sampling Period			Nephelometer Sampling Period			
			PM _{2.5}		PM ₁₀		Annual ^e	Fall Intensive ^f	Winter Intensive ^g	Annual ^e	Fall Intensive ^f	Winter Intensive ^g	Summer
			T/C	q/n	T/c	Q/n							
		<i>Minivol module -></i>	A ^h	B ⁱ	g ^k	h ^l							
SPE	Corcoran-Spear St. Station	Community Exposure									X		
SWC	SW Chowchilla	Interbasin Transport	FTC	FQN			X		X			X	
TEH2	Tehachapi Pass	Interbasin Transport, Visibility	FTC				X		X	X		X	
TEJ	Tejon Pass station	Interbasin Transport, Visibility								X			
VCS	Visalia Church St.	Community Exposure	FTC	FQN	TTC	TQN	(X)		X			X	
WAG	Walnut Grove tower station	Interbasin Gradient, Vertical Gradient								X			
WLKP	Walker Pass station	Interbasin Gradient, Visibility											X
YOD	Yoder Street	Fall Northern Edge of Source Area			TTC			X			X		
YOSE1	Yosemite National Park-Turtleback Dome	Boundary/Background, Visibility											
			-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
79		Total Number of Sites	35	29	16	11	41	11	25	26	22	27	5
		21 community exposure sites											
		4 intrabasin transport sites											
		7 interbasin transport sites											
		8 boundary/background sites											
		3 vertical gradient sites											
		16 visibility sites											
		17 intrabasin gradient sites											
		2 interbasin gradient sites											
		20 source-oriented sites											

(X) Includes the seven PM₁₀ sites operated during the annual program.

^a Teflon-membrane filter samples were analyzed for mass by gravimetry, filter transmission (b_{abs}) by densitometry, and elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Mo, Pd, Ag, Cd, In, Sn, Sb, Ba, La, Au, Hg, Tl, Pb, and U) by x-ray fluorescence (Watson et al., 1999); quartz-fiber filter samples were analyzed for anions (Cl⁻, NO₃⁻, SO₄²⁻) by ion chromatography (Chow and Watson, 1999), ammonium by automated colorimetry, water-soluble Na⁺ and K⁺ by atomic absorption spectrophotometry, and 7-fraction organic and elemental carbon (OC1 combusted at 120 °C, OC2 at 250 °C, OC3 at 450 °C, OC4 at 550 °C, EC1 at 550 °C, EC2 at 700 °C, and EC3 at 800 °C with pyrolysis correction) by thermal/optical reflectance (Chow et al., 1993b, 2001a); citric-acid-impregnated filter samples were analyzed for ammonia by automated colorimetry; and sodium-chloride-impregnated filters were analyzed for volatilized nitrate by ion chromatography.

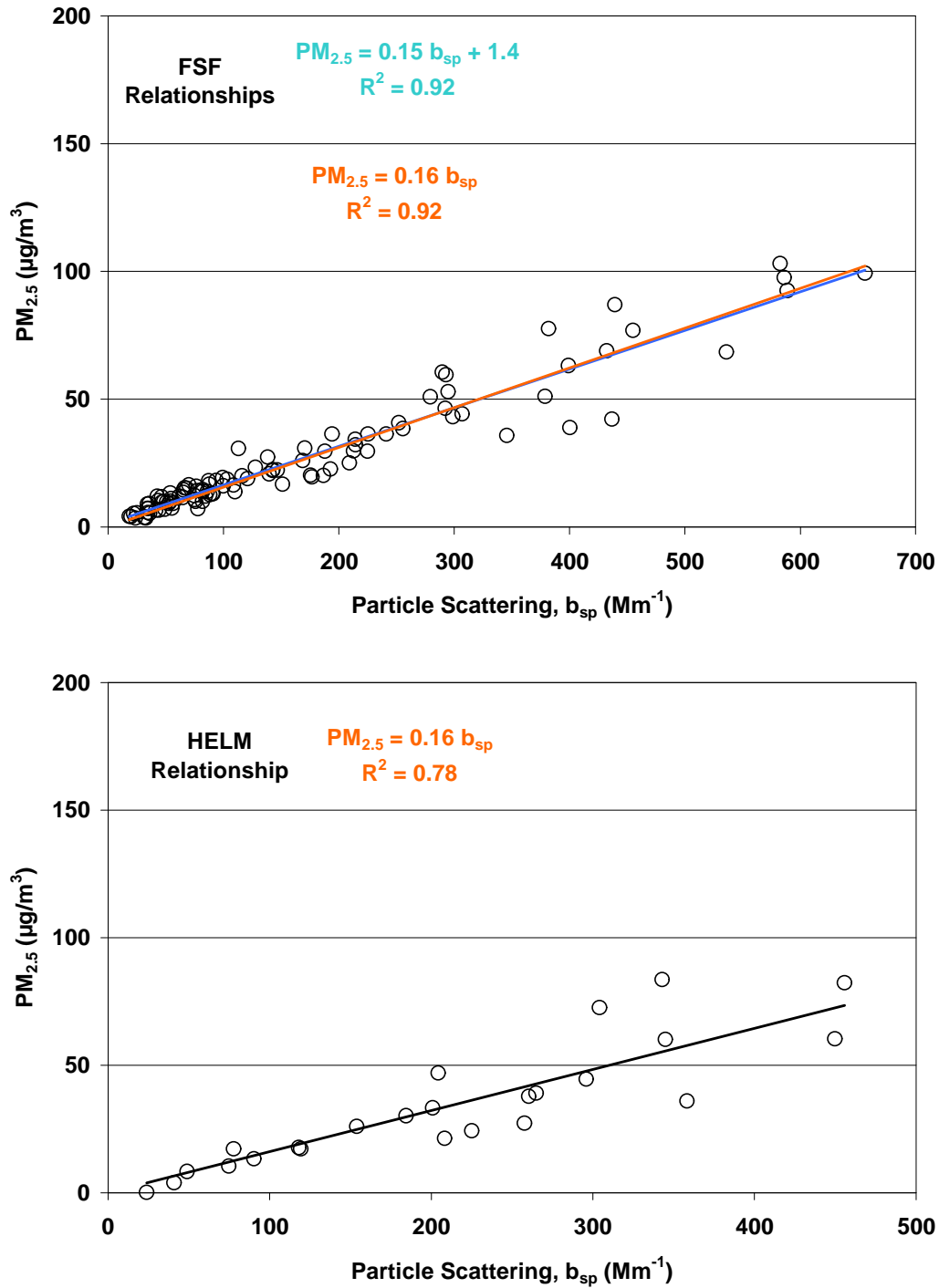
^b Satellite site annual sampling program included every-sixth-day 24-hour sampling at 35 PM_{2.5} sites and 7 PM₁₀ sites between 12/02/99 and 02/03/01. Particulate organic compounds were sampled at 20 sites between 02/06/00 and 01/31/01.

^c Satellite site fall intensive study included 24-hour sampling of PM₁₀ on 37 days between 10/09/00 and 11/14/00 at 11 sites. 6 sites (COP, H43, HAN, GRA, GRAS, and SFE) were equipped with both Teflon/citric acid and quartz/NaCl filter packs. 5 sites (CO5, DAIP, DAIU, ORE, and YOD) were equipped with only Teflon/citric acid filter packs.

^d Satellite site winter intensive study included 24-hour sampling of PM_{2.5} on 13 forecast episode days (12/15/00 to 12/18/00, 12/25/00, 12/27/00, 12/28/00, 01/04/01 to 01/06/01, and 02/01/01 to 02/03/01) at 25 PM_{2.5} sites, with 21 of the sites equipped with both Teflon/citric acid and quartz/NaCl filter packs.

- ^e Minivol module A: PM_{2.5} Teflon/citric acid filter packs at 35 satellite sites. Each filter pack consisted of a front Teflon-membrane filter (for mass, b_{abs}, and elements) backed up by a citric-acid-impregnated cellulose-fiber filter (for ammonia).
- ^f Minivol module B: PM_{2.5} quartz/NaCl filter packs at 29 satellite sites (same sites as module A but excluding ALT1, PAC1, KCW, EDI, CARP, and TEH2). Each filter pack consisted of a front pre-fired quartz-fiber filter (for ions and carbon) backed up by a sodium-chloride-impregnated cellulose-fiber filter (for volatilized nitrate).
- ^g Minivol module g: PM₁₀ Teflon/citric acid filter packs at 16 satellite sites, 4 of which (M14, VCS, COP, and OLD) were collocated with annual PM_{2.5} measurements, and 7 of which (M14, VCS, COP, FSD, BGS, HAN, and OLD) were annual PM₁₀ sites. Each filter pack consisted of a front Teflon-membrane filter (for mass, b_{abs}, and elements) backed up by a citric-acid-impregnated cellulose-fiber filter (for ammonia).
- ^h Minivol module h: PM₁₀ quartz/NaCl filter packs at 16 satellite sites, 4 of which were collocated with annual PM_{2.5} measurements (M14, VCS, COP, and OLD), and 7 of which (M14, VCS, COP, FSD, BGS, HAN, and OLD) were annual PM₁₀ sites. Each filter pack consisted of a front quartz-fiber filter (for ion and carbon analyses) backed up by a sodium-chloride-impregnated cellulose-fiber filter (for volatilized nitrate).
- ⁱ One of three anchor sites (ANGI, BAC, and FSF).
- ^j One of six sites (ALT1, PAC1, KCW, EDI, CARP, and TEH2) where only Minivol module A Teflon/citric acid filter packs were acquired.

Figure 1.1-3. Initial comparisons of particle scattering and PM_{2.5} concentrations at the Fresno First Street (FSF) urban and Helm (HELM) non-urban sites. Higher concentrations occurred during the winter and tend to deviate more from the linear regression relationship than those during other parts of the year. Nevertheless, there is a reasonably consistent relationship regardless of season.



those satellite sites without carbon measurements. As shown in Figure 1.1-4, light absorption by densitometry is predictable from EC, but only for $EC < 5 \mu\text{g}/\text{m}^3$ for measurements taken at Fresno during 2000. The left panels of Figure 1.1-4 show how the relationship becomes non-linear at high EC levels when the filters are very dark and Beer's Law ceases to apply. The right panels of Figure 1.1-4 show that 90% of the measurements are within a linear range that applies for $b_{\text{abs}} < 50 \text{ Mm}^{-1}$ and $EC < 5 \mu\text{g}/\text{m}^3$. Particle absorption efficiencies (slope) range from 11.4 to 12 m^2/g with correlations >0.9 for the three samplers in Figure 1.1-4. These particle absorption efficiencies are consistent with empirically derived values of $\sim 10 \text{ m}^2/\text{g}$ found by others (Trijonis et al., 1988; Horvath, 1993). This is a useful relationship for Federal Reference Method (FRM) samplers in the compliance network using Teflon filters that cannot be analyzed for carbon fractions by thermal methods. Similar comparisons will be made at the sites listed in Table 1.1-1, and the results will be summarized.

3.2.2.b Aethalometer Comparison

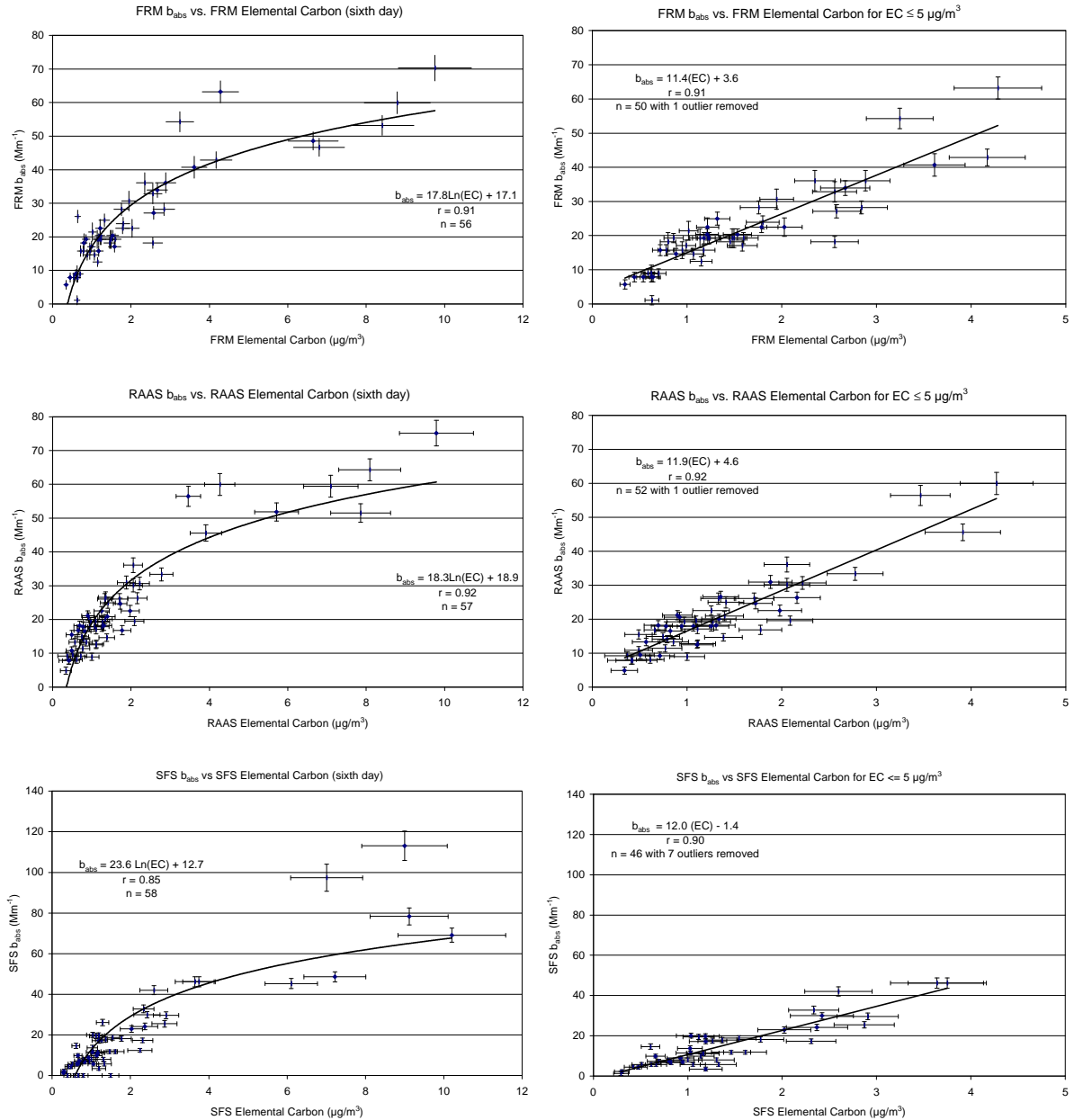
Compared to average FRM EC of $1.7 \pm 1.1 \mu\text{g}/\text{m}^3$, AETH1 and AETH7 report 25% and 31% lower BC, respectively. Pairwise comparisons between aethalometer BC and filter EC show comparability for AETH1 vs. RAAS, AETH1 vs. SFS, and AETH7 vs. SFS. With the exception of the AETH7 BC vs. RAAS EC comparison with a correlation of 0.89, all aethalometer BC and filter EC comparisons meet the criteria for predictability, but not for comparability or equivalence. The precisions from these measurements are good, ranging from 0.35 to 0.88 $\mu\text{g}/\text{m}^3$ for collocated precision and from 0.24 to 0.44 $\mu\text{g}/\text{m}^3$ for RMS precision.

To reconcile the difference between BC and EC measurements, the aethalometers' internal conversion factor 19.2 m^2/g that translates the measured light absorption to BC may need to be adjusted for different sampling locations (Lavanchy et al., 1999). Average BC/EC ratios range from 0.75 ± 0.21 (AETH7 vs. FRM) to 0.93 ± 0.26 (AETH1 vs. RAAS) in Table 1.1-5, indicating that aethalometer BC levels are lower than filter EC concentrations. This is consistent with other studies (Watson et al., 1991, 1996, 1998c; Lioussse et al., 1993; Babich et al., 2000). In comparisons of collocated BC vs. EC measurements in six urban areas, Babich et al. (2000) reported slopes ranging from 0.62 ± 0.04 to 0.83 ± 0.07 with high correlations ($r > 0.90$). Similar comparisons will be made at the other anchor sites, and the results will be summarized.

3.3 Task 1.1.3 – Nitrate Loss during Sampling and Analysis

The quartz-fiber/sodium-chloride-impregnated cellulose-fiber filter pack, preceded by anodized aluminum nitric acid denuders, measures non-volatilized nitrate from the front quartz-fiber filter and captures the volatilized nitrate dissociated from the front quartz-fiber filter with a backup sodium-chloride-impregnated cellulose-fiber filter. The sum of these two nitrate measurements in this filter pack represents total particulate nitrate in the atmosphere. Most nitrate will be in the gas phase (in the form of HNO_3) when ambient temperatures exceed 30 °C and in the particle phase (in the form of NH_4NO_3) at temperatures lower than 15 °C, with varying amounts of HNO_3 and NH_4NO_3 at intermediate temperatures.

Figure 1.1-4. Relationship between light transmission (b_{abs}) by densitometry from the Teflon-membrane filter and elemental carbon by Thermal/Optical Reflectance from the quartz-fiber filter for Federal Reference Method (FRM), Reference Ambient Air Sampler (RAAS), and Sequential Filter Sampler (SFS) samplers for samples acquired at the Fresno Supersite during 2000.



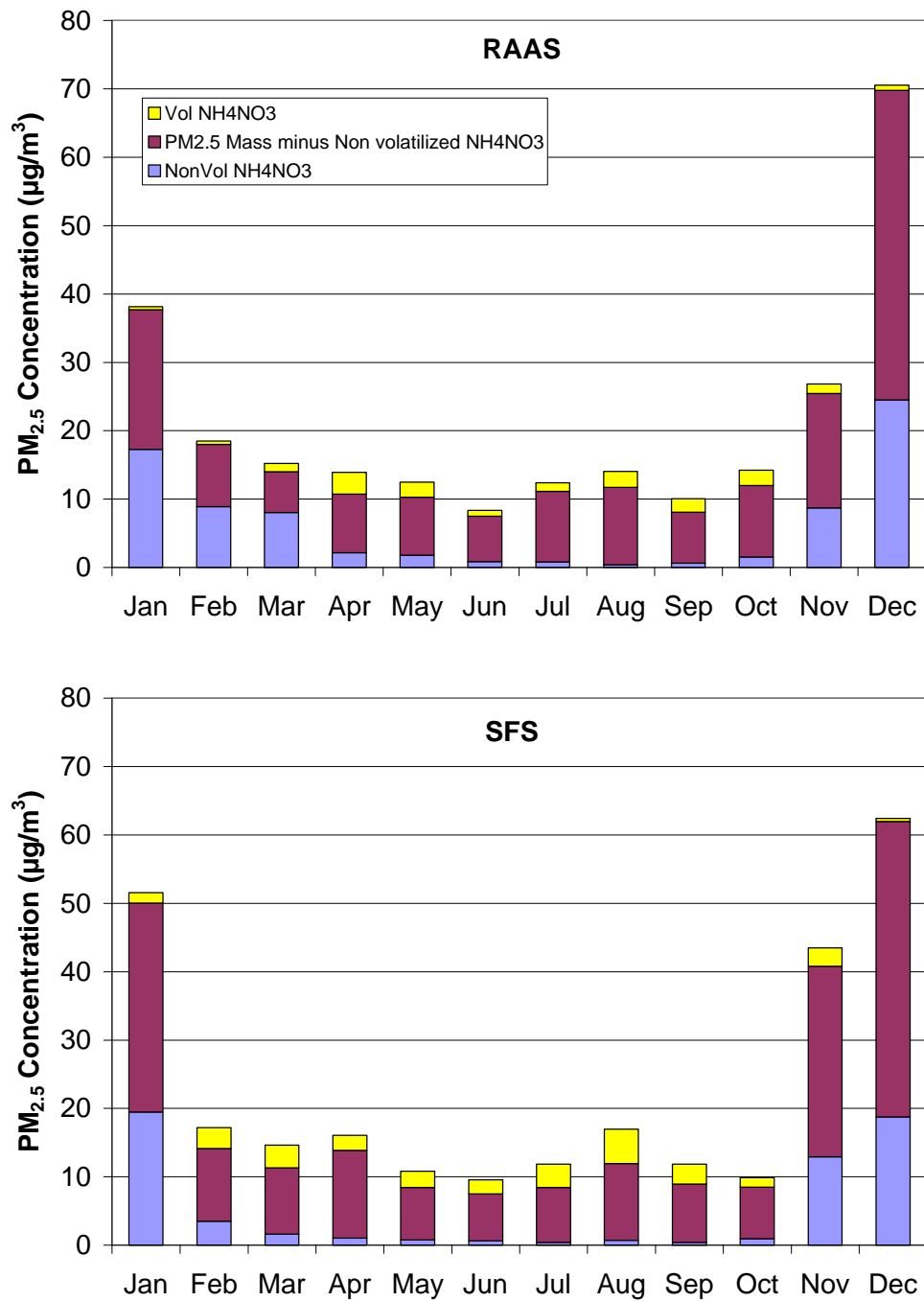
Relative humidity and concentrations of NH_3 and HNO_3 also affect gas/particle equilibrium, but temperature is by far the most important variable. When the air temperature changes during sampling, some of the nitrate already collected on the filter can volatilize. Nitric-acid-denuded total particulate nitrate should be greater than or equal to non-volatilized nitrate, depending on the extent of nitrate volatilization. An example of monthly nitrate volatilization for $\text{PM}_{2.5}$ samples acquired at the Fresno site is shown in Figure 1.1-5. Non-volatilized nitrate and volatilized nitrate were determined by sampling through a nitric acid denuder onto quartz-fiber and sodium-chloride-impregnated cellulose-fiber filters, respectively. This figure shows that nitrate volatilization varies from 3% to 9% during winter and from 70% to 90% during summer. Volatilized nitrate, assumed to be in the form of NH_4NO_3 , represents the $\text{PM}_{2.5}$ mass that is not measured gravimetrically on the Teflon-membrane filter.

Care has been taken during CRPAQS field operations to minimize nitrate losses during sampling and analysis by sealing each of the filter packs airtight, storing samples at $<4^\circ\text{C}$ temperature before and after sampling, and shipping/receiving samples in cold storage containers. Nitrate losses during sampling are assumed to be minimal in the $\text{PM}_{2.5}$ FRM samplers when ambient temperatures are $<30^\circ\text{C}$ because the FRM's sampling chamber temperature (where the filter is situated) is maintained at $\pm 5^\circ\text{C}$ of ambient temperature to minimize nitrate losses. Filter nitrate measurements from FRM samplers (available from the Fresno site only) will be compared with nitrate measurements from EPA speciation samplers, SFS, Minivols, and continuous nitrate monitors to evaluate when and where nitrate may be lost during or after sampling.

Passive sampling periods will also be examined. A study conducted in Mexico City (Chow et al., 2002) found that nitrate volatilization was significant, varying from 29% at 6-hour sampling sites to 53% at 24-hour sampling sites. Because the sample-changing schedule was every 24 hours at 6-hour sampling sites, and every 72 hours at 24-hour sampling sites, nitrate volatilization may have been somewhat enhanced by the longer passive period in the sampler, but this is not the main cause of different volatilization rates. Chow et al. (2002) shows that nitrate volatilization was 42% for samples taken during the afternoon periods (1200-1800 MST), 28% during late morning periods (0600 to 1200 MST), 9% during evening periods (1800 to 2400 MST), and 5% during early morning periods (0000 to 0600 MST). $\text{PM}_{2.5}$ total particulate nitrate was highest ($\sim 17\ \mu\text{g}/\text{m}^3$) during the morning when lower temperatures favored the particle phase. $\text{PM}_{2.5}$ nitrate was also high in the afternoon ($\sim 12\ \mu\text{g}/\text{m}^3$) when photochemical production of nitric acid was at its peak, but was attenuated by equilibrium favoring gaseous nitric acid at higher temperatures (Stelson and Seinfeld, 1982; Watson et al., 1994b). Very little nitrate ($<5\ \mu\text{g}/\text{m}^3$) was found during the nighttime and early morning periods. Correlation coefficients between non-volatilized and total particulate nitrate are near unity during evening and early morning periods, but decrease to 0.82 during afternoon periods.

The same diurnal accumulation of nitrate probably occurred at the 24-hour sites, but the higher-temperature air drawn through the filter during the afternoon probably volatilized much of the ammonium nitrate collected during the early- and late-morning periods. In this task, 24-hour samples will be compared to 5 times/day, 3-, 5-, and 8-hour samples to evaluate the effect of different passive sampling periods on nitrate volatilization.

Figure 1.1-5. Monthly average non-volatilized and volatilized ammonium nitrate compared to PM_{2.5} mass concentrations from Andersen Reference Ambient Air Samplers (RAAS) and DRI Sequential Filter Samplers (SFS) at the Fresno Supersite during 2000.



3.4 Task 1.1.4 – Adsorption of Gaseous Organic Carbon on Quartz-Fiber Filters

Certain organic compounds in suspended particles maintain a gas/particle equilibrium with their environments, similar to the situation for ammonium nitrate (Watson et al., 1994). Previous studies have found that either some volatile organic compounds evaporate from a filter (negative artifact) during sampling, or that some gaseous organic species are adsorbed (positive artifact) on quartz-fiber filters (Eatough et al., 1990; McDow and Huntzicker, 1990; Turpin et al., 1994). Several denuding and backup filter sampling systems can be applied to evaluate these artifacts, but they can be costly and inconclusive. Eatough et al. (1990) and Tang et al. (1994) concluded that desorption of organic gases from particles on the front quartz filter was the dominant sampling artifact (negative artifact) while Turpin et al. (1994) concluded that adsorption of organic gases by the front quartz filter was the dominant sampling artifact (positive artifact) for organic carbon. Turpin et al. (1994) recommended that a backup quartz-fiber filter behind the front Teflon-membrane filter be used to estimate the amount of organic gases which might adsorb onto quartz-fiber filters in the absence of particles.

A special experiment was set up at the Fresno Supersite to evaluate these negative and positive artifacts (Watson and Chow, 2001a). As shown in Figure 1.1-6, three channels in the Reference Ambient Air Sampler (RAAS) were configured with: 1) a double-stage Teflon/quartz filter pack, 2) a double-stage quartz/quartz filter pack, and 3) an organic gas denuder followed by a double-stage quartz/quartz filter pack to evaluate different approaches for estimating quartz filter organic gas adsorption. An XAD-coated glass denuder (URG Corporation, Chapel Hill, NC) was used from 01/01/00 to 06/30/00, and a charcoal-impregnated cellulose-fiber filter (CIF) parallel-plate denuder (Brigham Young University, Provo, UT) was used from 07/11/00 to 12/26/00. The XAD denuder (27 cm length \times 2.8 cm outside diameter) consists of four 0.2 cm thick \times 20 cm long concentric tubes spaced 0.2 cm apart and coated with washed XAD-4 resin (All Tech Associates Inc., Deerfield, IL) following the procedure developed by Gundel et al. (1995). The CIF denuder followed the design of Eatough (1999) (46.4 cm length \times 4 cm width \times 4 cm height) with 13 rectangular filter strips (24.5 cm length \times 3.7 cm width \times 0.41 mm thickness) (Schleicher & Schuell, Keene, NH) separated by 2-mm diameter aluminum rods. Denuders were cleaned, recoated, or replaced with unexposed CIF strips every one to two months.

Figure 1.1-7 shows how the three RAAS backup filter OC concentrations varied during year 2000 sampling. If the OC is due to denuder breakthrough, it should show lower values right after a denuder is reconditioned. Figure 1.1-7 shows no such systematic pattern. The CIF denuder is believed to have a large capacity, and both high and low values are seen soon after and long after it was replaced. These results are consistent with the hypothesis that most of the denuded backup is from volatilized particles. As such, denuded backup filter OC represents a lower limit for volatilized organic carbon because only those organic vapors with an affinity for quartz are adsorbed, and the backup filter may become saturated before all of those vapors are collected. If this is the case, then at least half of the $1.18 \mu\text{g}/\text{m}^3$ OC on the non-denuded quartz behind quartz filter represents SVOC that evaporated from the front filter deposit, and the true positive artifact is on the order of $0.5 \mu\text{g}/\text{m}^3$, well within the collocated precision estimates. This may explain why weighted sums of sulfate, nitrate,

crustal material, EC, and OC (e.g., Chow et al., 1993a, 1996) compare well with PM_{2.5} with front filter OC, but substantially underestimate the mass when backup OC is subtracted (assuming VOC adsorption on quartz fiber) and overestimate PM_{2.5} when backup OC is added (assuming particle volatilization from the front filter with partial re-adsorption on the backup filter). More analysis of adsorption of gaseous organic carbon will be conducted as data become available.

Figure 1.1-6. RAAS sampling system configuration for method evaluation at the Fresno Supersite.

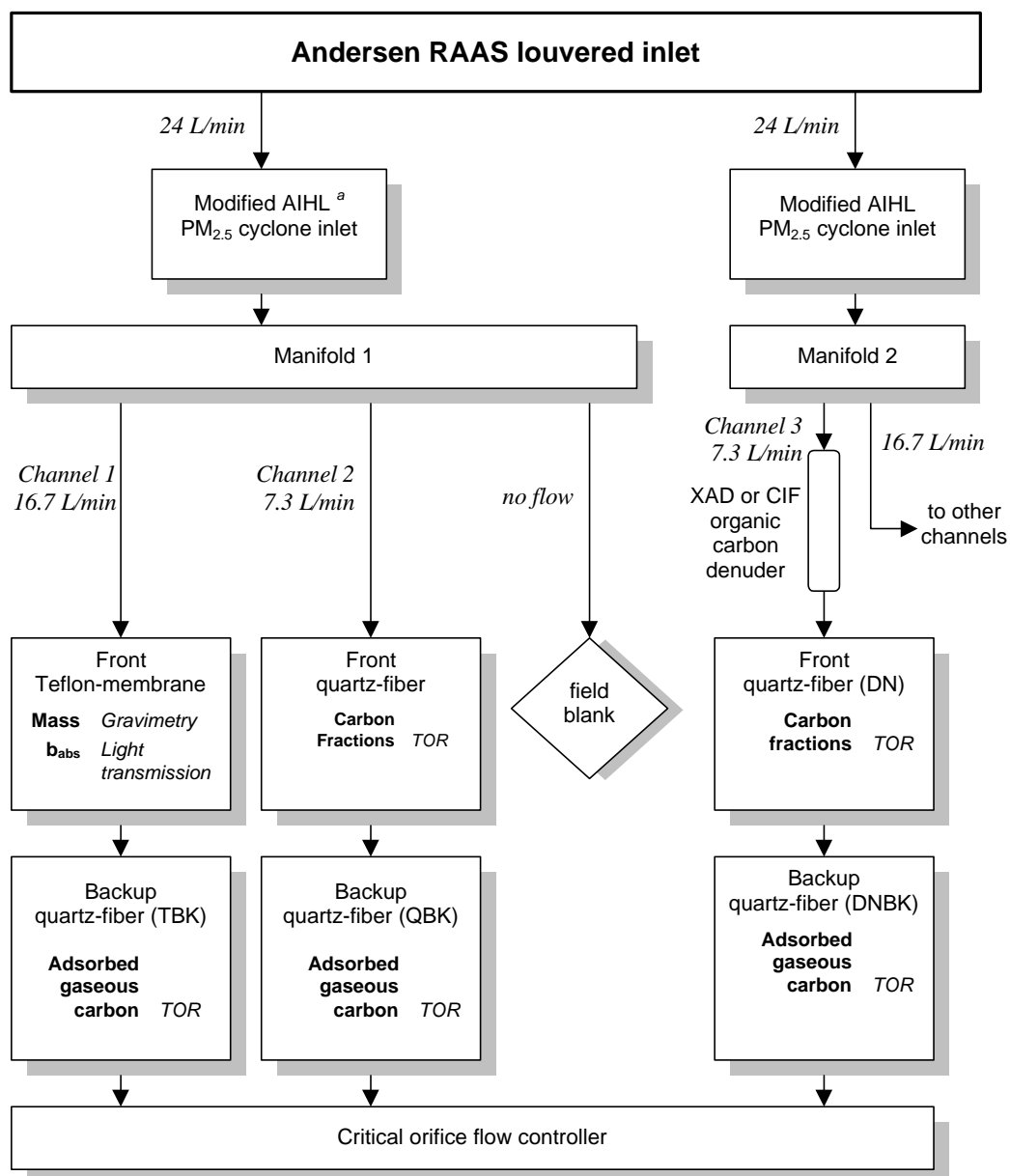


Figure 1.1-7. Temporal variations of RAAS speciation sampler quartz backup filter OC concentrations from: 1) non-denuded Teflon/quartz filter packs (TBK), 2) non-denuded quartz/quartz filter packs (QBK), and 3) denuded quartz/quartz filter packs, for samples acquired at the Fresno Supersite during 2000.

